PHYSICAL REVIEW E VOLUME 61, NUMBER 6 JUNE 2000

Molecular wall effects: Are conditions at a boundary ‘‘boundary conditions’’?

Howard Brenner and Venkat Ganesan
Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139-4307

(Received 21 December 1999)

This paper addresses and answers ‘‘no’’ to the question of whether the literal molecular-dynamically-derived species velocities prevailing at a solid surface bounding a two-component fluid continuum undergoing molecular diffusion constitute the appropriate species-velocity boundary conditions to be imposed upon the fluid continuum. In a broader context, generic boundary condition issues arising from the presence of different length scales in continuum-mechanical descriptions of physical phenomena are clarified. This is achieved by analyzing a model problem involving the steady-state diffusion of a dilute system of Brownian spheres (the latter envisioned as tractable models of solute ‘‘molecules’’) through a quiescent viscous solvent continuum bounded laterally by solid plane walls. Both physicochemical (potential energy) and hydrodynamic (steric) wall interaction effects experienced by the Brownian spheres are explicitly accounted for in our refined, microscale continuum model of the diffusion process. Inclusion of these ‘‘solid-wall–fluid’’ (*s-f*) boundary-generated forces [above and beyond the usual ‘‘fluid-fluid’’ (*f-f*) intermolecular forces implicit in the conventional Fick’s law macroscale continuum description] serves to simulate the comparable *s-f* molecular boundary forces modeled in molecular dynamics simulations of the diffusional process. A singular perturbation framework is used to clarify the physical interpretation to be ascribed to ‘‘continuum-mechanical boundary conditions.’’ In this same spirit we also clearly identify the origin of the physical concept of a ‘‘surface field’’ as well as of the concomitant surface transport conservation equation for strongly adsorbed species at solid walls. Our analysis of such surface phenomena serves to emphasize the fact that these are asymptotic, surface-excess, macroscale concepts *assigned* to a surface, rather than representing literal molecular material entities physically confined to the surface. Overall, this paper serves to illustrate the manner in which molecular simulations need to account for these different length scales and corresponding scale-dependent concepts if such analyses are to avoid drawing incorrect inferences regarding the molecular origins of continuum-mechanical boundary conditions.

PACS number(s): 68.45.Da, 46.15.Ff, 05.40.Jc

I. INTRODUCTION

A number of studies have appeared recently purporting to derive the boundary conditions to be imposed upon continuum-mechanical equations via ‘‘exact’’ molecular dynamics simulations of the appropriate physical scenario (see, for instance, [1–4]). Typically, such simulations involve computing the trajectories of molecules based upon a Langevin-type description of the molecular motion. During such calculations one computes the mean molecular motion averaged over a few molecular diameters near the ‘‘wall’’ (the solid wall being modeled in the simulations by a set of fixed lattice points interacting via potential-energy forces with the fluid molecules) to draw conclusions regarding the boundary conditions to be imposed at the wall upon the continuum-mechanical equations describing the transport phenomena.

At a continuum scale, however, one expects the boundary conditions to be explicitly dependent upon the particular continuum equation that purports to quantify the physical phenomenon being modeled. For instance, while the no-slip condition for pure fluids is a well-accepted boundary condition for viscous continua, it is also well known that an inviscid fluid continuum model cannot, on purely mathematical grounds, satisfy such a *vector* velocity boundary condition [5]. Thus, any statement regarding the boundary conditions derived by molecular dynamic simulations must logically be accompanied by an unequivocal elucidation of the explicit continuum equation to which such boundary conditions are intended to apply. It is quite clear, however, that despite the fact that molecular dynamics approaches can possibly yield detailed information about the exact statistical behavior of those fluid molecules moving in close proximity to a wall, such simulations cannot (at least to our knowledge) furnish the continuum equations themselves. Consequently, while the actual physical conditions prevailing at the boundary might, in fact, accurately accord with the inferences drawn from molecular dynamic simulations, such conclusions quantifying the literal ‘‘conditions at a boundary’’ are useless in the role of ‘‘boundary conditions’’ due to ignorance of the continuum-mechanical equations to which they are meant to apply. As such, it is necessary to clearly distinguish ‘‘conditions at a boundary’’ from ‘‘boundary conditions.’’

For instance, in a recent article [3] it is claimed that the boundary condition accompanying the convective-diffusive transport of a binary fluid mixture is one that demands that the *vector* velocities of both species individually satisfy no-slip conditions at the wall. This so-called ‘‘boundary condition’’ was derived by an exact simulation of the motion of molecules near the wall. For the purely diffusive case, where convection is absent, it is obvious that this boundary condition contradicts Fick’s law of molecular diffusion [6], at least in its usually accepted form—which excludes ‘‘external’’ forces and assumes the diffusion coefficient to be position independent. It might, however, be argued that Fick’s law is unlikely to be valid near the wall, where strong gradients due to solid-wall–fluid (s-f) interaction forces are likely to occur [7]. In such a case one might further argue that the no-slip species boundary condition needs to be applied to a refined microscale form of Fick's law, one which embodies ''molecular wall effects''—allowing for the variation of molecular diffusivity with distance from the wall as well as for the existence of short-range attractive or repulsive forces exerted on the fluid molecules by the wall. However, reiterating our earlier remarks, in the absence of information regarding the explicit form of this refined continuum-mechanical equation, the utility of such ''exact'' knowledge of the molecular ''conditions at the boundary'' is greatly diminished.

In the particular quiescent binary diffusion case to be studied in this paper, the fact that such exact knowledge (derived from simulations) is consistent with the known continuum-mechanical equations reinforces our claim regarding the inapplicability of the literal, molecularly derived conditions at the wall serving the role of boundary conditions to be imposed on the conventional macroscale continuum equations quantifying the phenomenon. Indeed, in some cases, such ''molecular wall effects'' might furnish conditions at the boundary that appear superficially consistent with the accepted continuum-mechanical boundary conditions, thereby leading to claims of having furnished a *molecular* ''proof'' of the appropriate continuum boundary condition (as in the case where the above-mentioned authors deal with the single-component fluid case [2]—namely, the classical no-slip fluid-mechanical boundary condition).

Paralleling the issues addressed in this paper, although only peripheral to our scaling argument context, is an extensive body of research concerned with the possibility of individual component ''slip'' occurring at solid boundaries for situations involving binary diffusion processes occurring among miscible species—typically gases—whose individual mass densities are unequal. This literature includes comprehensive reviews by Noever [8] and Jackson [9]. The latter deals at length with the original gaseous diffusion experiments of Graham [10], as well as with pertinent experiments by many others, including the comprehensive study by Kramers and Kistemaker [11]. An equally expansive theoretical [8,9,12–14] and simulation ([1,15]) literature exists on the topic, to cite only a few references thereto, and dates back as far as Maxwell [16]. Diffusion occurring in such systems, wherein gradients $\nabla\rho$ exist in the local total mass density ρ, necessarily induces a local convective velocity $\mathbf{v}$ ([12–14]), as is immediately evident from the overall continuity equation, $\partial\rho/\partial t+\nabla\cdot(\rho\mathbf{v})=0$. In contrast, our paper is concerned exclusively with situations wherein the total mass density is constant in both space and time. In such circumstances the ensuing diffusional process cannot give rise to convection, whence the fluid-mechanical velocity $\mathbf{v}$ is everywhere zero, including, of course, at the boundaries. As such, although this nonuniform density literature independently raises interesting questions regarding the fundamental issue of slip vs nonslip boundary conditions in diffusing systems, it does so in a context wholly different from that of the present paper. Even apart from the major distinction existing between compressible vs incompressible fluids, those studies do not deal with the issue of length scales [17], the central theme of the present study, in distinguishing between molecular ''conditions at a boundary'' and continuum ''boundary conditions.''

A. Philosophy

The explicit question addressed in this paper is whether or not the *literal* statistical-mechanical mean species-velocity fields existing at a boundary between a ''smooth'' solid surface and a fluid (as determined by molecular dynamic simulations) constitute the appropriate boundary conditions to be imposed on the comparable continuum fields appearing in a conventional transport equation description of the physical phenomenon. By using a particular example we demonstrate, at least in this one instance, that the answer to this question is ''no.'' This specific counterexample to what might otherwise seem a self-evident molecular dynamics inference suggests the need for caution in interpreting the results of such simulations in other contexts too. Using singular perturbation methods we demonstrate (albeit in the context of the elementary physical situation embodied in our illustrative example) that the fundamental source of the seemingly contradictory conclusion that ''conditions at a boundary'' are not ''boundary conditions'' lies in the disparity between the length scale l of the intermolecular forces appearing in the near-boundary simulation and the macroscopic length scale L characterizing the continuum physical phenomenon. Typically, the latter scale corresponds to a linear dimension of the experimental apparatus normal to the wall.

Molecular dynamic modeling of physical phenomena involving fluid-solid boundaries needs to address, at a minimum, at least different three length scales: (i) the length scale l_{ff} of the fluid-fluid interactions between the fluid molecules [18]; (ii) the length scale l_{sf} of the interactions between the molecules of the solid wall and those of the fluid; and (iii) the macroscopic length scale L (normal to the solid wall) of the physical apparatus within whose boundaries the simulations are intended to apply. (Typically, L would be either the distance between two planar walls bounding the fluid laterally on either side of a fluid-filled gap, or the radius of a circular tube containing the fluid.) In most circumstances the two molecular length scales l_{ff} and l_{sf} will be comparable in magnitude, in which case we will denote their common magnitude by the single symbol l: $\{l_{ff},l_{sf}\}\equiv l$ [19].

The fundamental difference between the latter intermolecular length scale l and the apparatus length scale L is that the former is intrinsic to the physicochemical molecular constitutions of the solid wall and fluid phases, independently of the dimension L of the apparatus in which the transport experiment is being conducted. In contrast, the length scale L is an extrinsic variable under the control of the investigator, independently of the molecular constitution of either the solid or fluid phases. An ''exact'' $(l\oplus L)$-scale model of the physics quantifying the whole system—either exact in a molecular dynamics sense or exact in a refined microcontinuum-mechanical sense to be discussed—will necessarily embody both the intermolecular f-f and s-f length scales l, as well as the apparatus length scale L. As such, the literal molecular dynamic conditions prevailing at the boundaries of the system would be the same as the boundary conditions satisfied by this refined $(l\oplus L)$-microscale continuum model, whence no distinction would exist between the two.

The differential equations quantifying conventional macroscale continuum-mechanical models, applicable on the length scale L, while implicitly embodying the intermolecular *f-f* forces, do not incorporate the effects of the *s-f* forces—either explicitly or implicitly. This is evident from the fact that the constitutive relations [20] that enter into classical continuum-mechanical formulations are concerned only with the *f-f* aspect of the problem. As such, these conventional macroscale descriptions of the physical phenomena fail to embody the correct physics in regions of thickness $O(l)$ near the wall, where the *s-f* forces are of at least equal importance to the *f-f* forces. (Indeed, the *s-f* forces in that region may be dominant over the *f-f* forces, as, for example, in the case of ''adsorption'' phenomena—see Sec. III.)

It is precisely because of this failure to incorporate *s-f* forces that one needs to supplement conventional L-scale macrocontinuum equations with appropriate L-scale ''boundary conditions'' [21]. However, even when supplemented in this manner, such continuum-mechanical descriptions still do not represent the correct (i.e., molecularly derived) physics in the neighborhood of the boundaries, namely, at distances from the boundary of $O(l)$. The simple reason for this failure is that macroscale continuum-mechanical descriptions are generally incapable of resolving phenomena on molecular length scales. Only ''exact'' $(l\oplus L)$-scale descriptions, namely, those microcontinuum or molecular dynamic descriptions that properly embody physical phenomena occurring on all length scales between l and L, are capable of encapsulating the exact physics [22]. At best, by invoking an appropriate boundary condition, the solution of the conventional *f-f* continuum-mechanical equations satisfying this boundary condition will nevertheless only be *asymptotically equivalent* to the exact solution in a singular perturbation sense, but not in a truly equivalent physical sense as regards fine-scale behavior near the boundaries. No single L-scale boundary condition can ever fully compensate for the loss of detailed l-scale physical molecular information about the *s-f* (or possibly even the *s-s*) interactions implicit in such a coarse-scale description.

Because of limitations imposed by currently available computational resources, contemporary molecular dynamic simulations are capable of addressing only those situations for which the apparatus length scale L is of the same order of magnitude as l. This is evident from the fact that in such simulations [1–4] distances normal to the boundary are invariably rendered dimensionless with intermolecular distances l. By doing so, such simulations implicitly limit themselves to situations in which $l/L=O(1)$. In contrast, conventional macrocontinuum-mechanical descriptions of transport phenomena apply only in circumstances where $l/L\ll 1$. It is because of the wide disparity between these two regimes, coupled with the generally singular nature of perturbation solutions of the exact $(l\oplus L)$-microscale problems in the limit of $l/L\rightarrow 0$, that molecular dynamic calculations of the conditions at a boundary do not bear a one-to-one correspondence with the boundary conditions to be imposed on conventional *f-f* continuum models of the phenomena, except perhaps fortuitously (as we believe to be the case for the classical no-slip fluid-mechanical velocity boundary condition for single-component systems [2]). Stated explicitly, the correct limiting behavior of the pertinent fields proximate to solid boundaries cannot be obtained by effectively setting $L=\infty$ at the outset of the calculations and subsequently focusing exclusively on the l-scale behavior.

In the generic terminology of singular perturbation theory [23–28], and in relation to the magnitude of the small perturbation parameter $l/L=\delta$, say, current molecular dynamic simulations of phenomena occurring near boundaries furnish the numerical equivalents of the leading-order (zero-order) ''inner'' or boundary-layer-like fields, where distances normal to the boundary are scaled with l. In contrast, conventional continuum equations furnish only the corresponding (zero-order) ''outer'' or bulk fields, where distances normal to the boundary are scaled with L. In the usual way with such singular perturbation analyses, the requisite asymptotic matching conditions between these two asymptotic limiting fields in the limit $\delta\rightarrow 0$ serve to furnish the appropriate boundary conditions to be imposed on the outer fields. And it is precisely because this boundary condition is an asymptotic *matching* condition, rather than a *literal* condition prevailing at the actual physical solid-fluid boundary, that current molecular dynamics simulations furnish conditions at a boundary that are generally inconsistent with conventional continuum-mechanical boundary conditions. On the other hand, were such simulations ever to reach the stage where they were computationally capable of dealing with the $l/L \ll 1$ case, rather than being limited to the $l/L=O(1)$ case, the potential inconsistency would presumably disappear. In such circumstances, in order to capture the underlying physics (albeit ''far'' from boundaries in terms of the length scale l), one would no longer require conventional *f-f* macroscale continuum-mechanical descriptions of the phenomena, together with their concomitant need for constitutive equations, phenomenological coefficients, and macroscale boundary conditions. However, that day appears to lie far in the future. And even then, it is difficult to imagine a scenario in which continuum mechanics would no longer prove useful for at least qualitatively interpreting the gross behavior of complex fluid-mechanical phenomena. Moreover, moving beyond zero-order macroscale descriptions, first-order corrections to these classical zero-order results should be able to furnish systematic tools for rationally analyzing situations from a continuum viewpoint, in which terms of order l/L, though small, are nevertheless sufficiently sensible to require an accounting in quantifying the basic physics.

In the short term, ''hybrid'' computations [29,30]—which combine both discrete molecular and continuum-mechanical approaches, albeit in an *ad hoc* manner—appear to offer the best hope for reconciling molecular dynamics with continuum mechanics.

B. Outline

The following sections address a simple physical problem, namely, the nonconvective transport of noninteracting Brownian particles diffusing through an otherwise quiescent viscous liquid bounded laterally by a pair of solid plane walls. In an attempt to mirror the main molecular *s-f* wall physics via a continuum model, we explicitly incorporate the physicochemical and hydrodynamical interaction forces occurring between the solid wall and the binary fluid system into an $(l\oplus L)$-scale microcontinuum-mechanical constitutive equation for the solute flux which embodies several simple refinements of the conventional L-scale macrocontinuum Fick's law flux relation.

The physically plausible constitutive form adopted for this ''exact'' microscale model is designed to mirror the essential l-scale features implicitly present in the molecular dynamics description [3] of the near-wall diffusion phenomena, particularly the vanishing of the individual species solute and solvent component velocities along the wall, and the existence of short-range steric repulsive forces occasioned by the impenetrability of the wall. At the same time, this model faithfully reproduces classical L-scale, Fick's law behavior ''far'' from the wall—namely, at distances large compared with l. This exact, $(l\oplus L)$-scale microcontinuum model is then used to illustrate a fundamental macrocontinuum-mechanical concept that—though implicitly assumed in all analyses—is rarely, if ever, explicitly stated. This relates to the issue of the (macroscale) boundary conditions to be imposed on the conventional Fick's law L-scale continuum description. Explicitly, the existence of the microscale model serves to initiate a formal singular perturbation scheme to identify appropriate inner l-scale and outer L-scale expansions, in addition to identifying the spatial region relative to the walls within which conventional continuum-mechanical equations would be expected to apply. Further, we also establish the boundary conditions applicable to this classical Fick's law description of the diffusional process. In particular, such boundary conditions are shown to arise from the requisite asymptotic $\delta\rightarrow 0$ matching condition between the respective inner limit of the outer fields and the outer limit of the inner fields.

This singular perturbation approach underlies all continuum-mechanical interpretations of macroscale boundary conditions [31–33]. We argue that any approach that fails to address the presence within the underlying physics of the two disparate length scales l and L will, except for fortuitous circumstances, necessarily fail to furnish the correct L-scale boundary conditions. In a later section we briefly consider a closely related issue which is also purely asymptotic in nature, namely, the concepts of surface-excess fields and concomitant surface-excess transport processes arising from preferential ''adsorption'' of the solute at the wall relative to the solvent. The existence of this additional surface feature serves to further reinforce our generic arguments about the current limitations of molecular dynamic simulations. During the course of this adsorption analysis we identify the origins of such surface (more properly termed ''surface-excess'') phenomena as again arising from the existence of different length scales, in this case the large disparity existing in the magnitudes of the respective solute and solvent s-f forces [characterized, say, by the respective length scales $(l_{sf})_{\text{solute}}$ and $(l_{sf})_{\text{solvent}}$] exerted by the wall on the two different molecular species comprising the binary fluid continuum. We argue that these surface-excess concepts are not purely molecular scale in origin (i.e., purely inner-scale conceptions). Rather, they are strictly macroscale notions, arising from the need to account for the slack existing between the outer (continuum-mechanical) L-scale and the exact $(l\oplus L)$-scale descriptions of the physical phenomena. We point out the existence of paradoxes arising when one erroneously attempts to construe these surface adsorption phenomena as being purely molecular, l scale, near-wall concepts. These paradoxes are eventually resolved by considering the issue of the very different length scales involved. Their resolution further serves to clarify the origins of surface fields as arising from the fundamental scaling issue—whereby the ''strength'' of the adsorptive wall-interaction forces is shown to be a relative rather than absolute concept. That is, all other things being equal, the extent of the adsorption depends upon the dimension L of the container within which the adsorption process occurs, except in the asymptotic limit $l/L\rightarrow 0$. It is only in the latter case that the phenomenon of adsorption becomes an intrinsic physicochemical property, attributable solely to the molecular-level interactions between the wall, solute, and solvent.

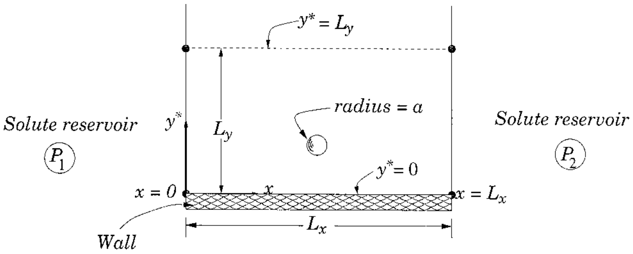

FIG. 1. Depiction of the lower half of the diffusion cell (not drawn to scale). L_x and $2L_y$ represent the length and width of the cell, respectively, in the x and y^* directions. Also shown is a Brownian sphere of radius a.

II. WALL EFFECTS ON BINARY DIFFUSION

A. Problem description

As in Fig. 1, we consider a steady-state diffusional process occurring within a diffusion cell, arising from a prescribed solute concentration difference maintained between the two ends the cell. The cell (whose lower half is shown in Fig. 1) consists of (i) two smooth plane parallel walls separated by a distance $2L_y$ in the y^* direction, which bound the fluid laterally; and (ii) a pair of solute/solvent reservoirs separated by a distance L_x, which bound the fluid longitudinally. We suppose in what follows that $2L_y\sim O(L_x)$, so that the single symbol $L\equiv L_y$ can be used to characterize the length scale of the entire apparatus. The fluid housed within the cell consists of a mobile binary system composed of a dilute suspension of (colloidally and hydrodynamically) noninteracting, neutrally buoyant, rigid Brownian spheres (solute ''molecules'') of radius a dispersed in an incompressible viscous Newtonian fluid continuum (the solvent) of viscosity μ. The purely fluid (f-f) portion of the system is assumed to be thermodynamically ''ideal.'' By virtue of the geometric symmetry of the parallel wall system, coupled with the finite size of the Brownian spheres, it suffices to limit attention to the range $L_y>y^*\geqslant a$ as regards the spatial distribution of the (centers of the) Brownian particles.

The microscale constitutive model equation ultimately adopted for the exact solute flux incorporates the s-f wall-fluid interaction effects on the transport of those solute molecules moving in proximity to the walls, as well as displaying classical f-f fluid behavior far from the walls. This introduces two disparate length scales into the problem, viz., the molecular range l of the wall interaction forces, and the apparatus length scale L. We then elaborate the singular perturbation scheme that arises from the incongruity of these two length scales. Elucidation of the requisite matching conditions between these will be shown formally to furnish the macroscale boundary conditions to be imposed on the outer, Fick's law–level diffusion equation governing the macroscale solute transport process.

As pointed out in the Introduction, conventional continuum-mechanical transport equations (whether derived by statistical-mechanical arguments [34] or simply postulated on the basis of macroscopic conservation principles together with appropriate constitutive models) generally embody only *f-f* forces, and implicitly entail the assumption of only relatively *weak* inhomogeneities in the physical fields. As such, this continuum description does not include the steep species gradient effects encountered near the wall, arising from the *s-f* interactions. Indeed, for a given fluid, such interactions may depend quantitatively upon the specific physicochemical constitution of the wall itself, as occurs in the case of adsorption phenomena. Explicit incorporation of these ''molecular wall effects'' requires refining the classical Fick's law description of the diffusional process so as to explicitly take account of these *s-f* forces. In this context we use a simple embellishment of Fick's law to model the transport of the Brownian molecules, which are subject to both steric hydrodynamic wall effects and potential-energy wall interaction forces. This microscale refinement (i) explicitly introduces a potential whose gradient represents the physicochemical interaction force between the wall and a Brownian solute particle; and (ii) incorporates a position-dependent and transversely isotropic diffusivity tensor **D** (in place of the usual position-independent and isotropic Stokes-Einstein diffusivity $D_\infty = kT/6\pi\mu a$), one whose components normal and parallel to the wall depend upon the distance y^* of the center of the Brownian sphere from the wall [35]. Both of these two wall-induced modifications are regarded as arising from *s-f*-type forces, inasmuch as each originates from an interaction between the solid wall and the Brownian solute molecules. The conventional *f-f* Fick's law description does not incorporate such forces into its formulation.

The wall-interaction potential, denoted by E (the latter representing the physical potential rendered dimensionless with kT), is assumed to vary only in a direction normal to the wall, and to asymptotically attain a constant limiting value E_∞ at distances from the wall that are large compared with molecular dimensions. Explicitly,

$$E(y^*) \to E_\infty = \text{const} \quad (y^* \gg l). \tag{1}$$

This potential-energy function is characterized by a molecular length scale l; that is, E or, more precisely, $E - E_\infty$, is sensible only in the region $y^* = O(l)$. As such, E is functionally of the form $E \equiv E(y^*/l)$. Typical potential-energy profiles for both adsorbing and nonadsorbing solute molecules are illustrated in Fig. 2. Subsequent discussion, however, eschews the need for choosing any explicit functional form for the potential-energy function.

Based on the above physical description, we model the macroscopically steady transport of the diffusing Brownian particles using a Smoluchowski framework [36]:

$$\nabla \cdot \mathbf{J} = 0, \tag{2}$$

in which **J** denotes the flux density of the Brownian particles relative to the fixed walls. This flux is assumed to possess the constitutive form

$$\mathbf{J} = -\mathbf{D} \cdot \nabla P + \mathbf{M} \cdot \mathbf{F} P, \tag{3}$$

where $P \equiv P(x, y^*)$ denotes the probability density for the center of a Brownian particle to be situated at the point (x, y^*). The field P is equivalent to a corresponding volumetric solute number density concentration field on the assumption that the system is sufficiently dilute so as to behave ideally in a physicochemical sense, in which circumstances the number density and probability density may be used interchangeably, modulo a normalization factor. In the above, **D** and **M** respectively denote the tensor diffusivity and mobility of a diffusing Brownian particle. The vector force field $\mathbf{F} \equiv F(y^*)\hat{\mathbf{y}}$, with $F = -kT\, dE/dy^*$ and $\hat{\mathbf{y}}$ a unit vector in the y^* direction, represents the interaction potential-energy force exerted by the wall on a Brownian sphere whose center lies at a distance y^* from the wall.

The diffusivity and mobility of the Brownian spheres have been assumed to be tensorial in nature rather than scalar so as to quantify the anisotropy arising from the proximity of a sphere to the plane wall [37]. We suppose, based upon the geometric symmetry of the sphere–plane-wall configuration, requiring these tensors to be transversely isotropic with regard to the direction normal to the wall, that

$$\mathbf{D} = D_\parallel[(y^* - a)/a]\hat{\mathbf{x}}\hat{\mathbf{x}} + D_\perp[(y^* - a)/a]\hat{\mathbf{y}}\hat{\mathbf{y}}, \tag{4}$$

and

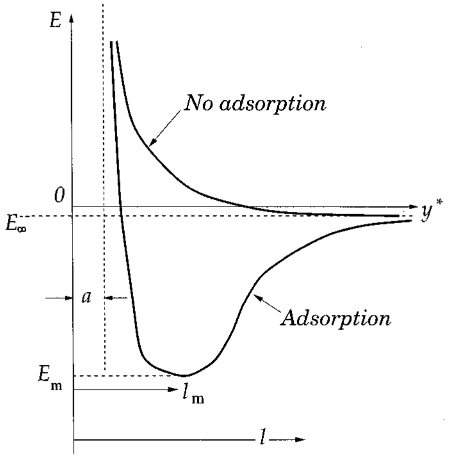

FIG. 2. Typical potential-energy profiles experienced by the Brownian sphere, illustrating (i) the short-range impenetrability of the wall to the rigid sphere; (ii) the asymptotic limit E_∞ (presumably achieved well before the sphere center reaches the midpoint between the two walls); (iii) the essentially monotonic approach of the potential to its limiting value in the absence of solute adsorption; and (iv) the existence of a potential-energy minimum E_m in circumstances where solute adsorption occurs. As discussed by Shapiro, Brenner, and Guell [58] [see also Eq. (69)], the subsequent theory requires that the integral $\int_a^\infty dy^* \{\exp[E_\infty - E(y^*)] - 1\}$ be convergent. The nonadsorbing case arises when the nature of the potential-energy function is such that the above integral is of $O(l)$, whereas adsorption occurs when the integral is of $O(L)$.

$$\mathbf{M}=M_{\parallel}[(y^{*}-a)/a]\hat{\mathbf{x}}\hat{\mathbf{x}}+M_{\perp}[(y^{*}-a)/a]\hat{\mathbf{y}}\hat{\mathbf{y}}. \tag{5}$$

The arguments of the latter pair of expressions explicitly indicate the functional dependence of **D** and **M** upon the distance $y^{*}-a$ of the closest point on the Brownian sphere from the wall [38]. Since wall effects become negligible far from the wall(s), the following asymptotic behavior prevails:

$$D_{\parallel}, D_{\perp} \rightarrow D_{\infty}=\text{const} \quad (y^{*} \gg a). \tag{6}$$

Furthermore, in view of the Nernst-Planck relationship existing between the diffusivity and mobility tensors, namely [39,40],

$$\mathbf{D}=kT\mathbf{M}, \tag{7}$$

similar asymptotic behavior also holds for $M_{\parallel}$ and $M_{\perp}$.

Based upon hydrodynamical considerations involving the singular nature of the hydrodynamic lubrication forces for a spherical particle in contact with a solid plane wall [37], requiring that $\mathbf{M}=\mathbf{0}$ at $y^{*}=a$, we have that [41]

$$D_{\parallel}, D_{\perp} \rightarrow 0 \quad \text{for } y^{*}-a \rightarrow 0. \tag{8}$$

This property requires that a Brownian particle be diffusionally immobile when in contact with the wall despite the existence of a macroscopic solute concentration gradient in the x direction for all y^{*}, including the ''wall,'' $y^{*}=a$. Use of the above limiting property in Eq. (3) yields

$$\mathbf{J}(x, y^{*}=a)=\mathbf{0}. \tag{9}$$

The generic relations between the solute diffusion flux **J** and the solute species velocity **v** (not to be confused with the fluid-mechanical velocity, which is zero in the present circumstances) is $\mathbf{J}=P\mathbf{v}$ [42]. Accordingly, since P is necessarily everywhere finite, the preceding equation requires that [43]

$$\mathbf{v}(x, y^{*}=a)=\mathbf{0}. \tag{10}$$

The latter species-specific, no-slip, exact $(l \oplus L)$-scale condition at the boundary is identical with the l-scale species-velocity ''boundary condition'' (so called) proposed in a recent molecular dynamics study of transport in binary convective-diffusive systems [3]. However, we argue below that the above exact condition, which arises from *s-f* forces (and hence should be construed as a ''wall effect''), does not, in fact, constitute the appropriate species-specific boundary condition to be imposed on the conventional L scale Fick's law formulation of the solute diffusion problem, which addresses only *f-f* forces. Rather, the appropriate macroscale boundary condition is eventually to be determined as an asymptotic *matching condition* imposed upon the classical Fick's law macrocontinuum equation—the so-called outer equation—so as to enable a smooth interpolation with the l-scale inner equation (the latter including *s-f* forces).

This program underlines our main objective in this particular example, namely, that of illustrating the singular consequences arising from the existence of disparate scales occasioned by the presence of the bounding walls. Numerical simulations adjoining the wall probe only the physics of the ''inner'' region, $y^{*}=O(l)$. In contrast, conventional continuum-mechanical equations are valid only in regions far removed far from the boundaries, namely, only in the ''outer'' region, $y^{*}=O(L)$, and there constitute the so-called outer equations. In the following, we utilize singular perturbation techniques to explicitly identify the existence and location of these two distinct regions, as well as to establish the pertinent transport equations and boundary conditions appropriate to each.

B. Nondimensionalization

Utilizing the above data regarding the constitutive forms of the various quantities appearing in Eq. (3), Eq. (2) reduces to

$$D_{\parallel}\frac{\partial^{2}P}{\partial x^{2}}+\frac{\partial}{\partial y}\left[D_{\perp}\left(\frac{\partial P}{\partial y}+P\frac{dE}{dy}\right)\right]=0. \tag{11}$$

The latter represents a steady-state microscale diffusion equation, one which explicitly and exactly incorporates all of the $(l \oplus L)$-scale continuum-level *f-f* and *s-f* interactions in a simple, albeit physically plausible, manner [44]. This equation is to be supplemented by the no-normal-flux boundary condition, $J_{y}(x, y^{*}=a)=0$, arising from the impermeability of the wall to solute transport. Equivalently, we require that

$$D_{\perp}\left(\frac{\partial P}{\partial y^{*}}+P\frac{dE}{dy^{*}}\right)=0 \quad \text{at } y^{*}=a \quad (\forall x), \tag{12}$$

together with the prescribed uniform solute concentrations maintained at the two ends of the cell:

$$\begin{gathered} P(x=0, y^{*})=P_{1}=\text{const}; \\ P(x=L_{x}, y^{*})=P_{2}=\text{const} \quad \forall(L_{y}>y^{*}>a). \end{gathered} \tag{13}$$

It will prove convenient to work henceforth with dimensionless equations. This nondimensionalization is effected as follows. Imagine that each of the independent and dependent variables appearing in the preceding dimensional equations is augmented by affixing a superscript asterisk to it (as we have already done explicitly for the dimensional distance y^{*} from the wall). We then define the dimensionless counterparts of these dimensional variables as follows (with P_{0}^{*} a characteristic solute concentration):

$$\begin{gathered} x=x^{*}/L_{x}, \quad y=(y^{*}-a)/L_{y}, \quad P=P^{*}/P_{0}^{*}, \\ D=D^{*}/D_{\infty}^{*}, \end{gathered} \tag{14}$$

$$J_{x}=J_{x}^{*}L_{x}/D_{\infty}^{*}P_{0}^{*}, \quad J_{y}=J_{y}^{*}L_{y}/D_{\infty}^{*}P_{0}^{*}. \tag{15}$$

(For physical clarity in the analysis which follows, we will retain the nondimensional symbol $D_{\infty}=D_{\infty}^{*}/D_{\infty}^{*}\equiv 1$ in subsequent equations.) Additionally, it will prove convenient to further define the following nondimensional length-scale parameters:

$$\epsilon \overset{\text{def}}{=} a/L_{y} \quad \text{and} \quad \delta \overset{\text{def}}{=} l/L_{y}. \tag{16}$$

Observe in the above nondimensionalizations that the value $y=0$ corresponds to (the surface of) a Brownian particle being in contact with the wall, and that the dimensionless distance y normal to the wall straddles the range $\epsilon^{-1}-1 \geqslant y > 0$. Accordingly, we note for later reference that y ranges over the values $\infty > y > 0$ in circumstances where $\epsilon \rightarrow 0$.

Upon rewriting the trio of equations (11)–(13) in terms of these dimensionless variables, they become

$$D_{\parallel}(\epsilon^{-1}y)\frac{\partial^2 P}{\partial x^2}+\frac{\partial}{\partial y}\left[D_{\perp}(\epsilon^{-1}y)\left(\frac{\partial P}{\partial y}+P\frac{dE(\delta^{-1}y)}{dy}\right)\right]=0, \tag{17}$$

$$P(x=0,y)=P_1=\text{const}; \quad P(x=1,y)=P_2=\text{const}, \tag{18}$$

and

$$J_y \equiv -D_{\perp}(\epsilon^{-1}y)\left(\frac{\partial P}{\partial y}+P\frac{dE(\delta^{-1}y)}{dy}\right)=0 \quad \text{at } y=0. \tag{19}$$

Given the diffusivity and potential-energy phenomenological data required in the above equations, together with prescribed values of P_1 and P_2, it can be shown mathematically that the preceding trio of equations uniquely determine the exact $(l \oplus L)$-scale fields $P(x,y)$ and $\mathbf{J}(x,y)$.

Hydrodynamic considerations arising from the vanishing Brownian sphere mobility components at the wall dictate that

$$\mathbf{J}(x,y=0)=\mathbf{0} \tag{20}$$

[cf. Eq. (9)]. In view of the fact that Eq. (19) already requires that $J_y(x,y=0)=0$, the only new condition demanded by Eq. (20) is

$$J_x \equiv -D_{\parallel}(\epsilon^{-1}y)\frac{\partial P}{\partial x}=0 \quad \text{at } y=0. \tag{21}$$

It is important to observe that this latter relation does not *per se* constitute a ''boundary condition'' at the wall, since the only boundary condition imposed on the exact system of equations at the wall is that specified by Eq. (19). Rather, it represents a ''condition at a boundary,'' a condition which arises strictly as a consequence of what might aptly be termed ''molecular wall effects.'' Given the role of the Brownian particles as ''molecules,'' this phraseology appears entirely appropriate.

Specification of a tangential flux component J_x at the wall, as in Eq. (21), as a condition to be imposed on the solution of the trio of equations (17)–(19), will generally overspecify the boundary data defining the boundary value problem, and hence result in a nonexistent solution for $P(x,y)$. That such overspecification in present circumstances does not result in nonexistence is trivially a consequence of the fact that $D_{\parallel}=0$ at $y=0$. Any value of this diffusivity component other than zero would fail to lead to an existent solution (see, for example, the Davis, Kezirian, and Brenner tangential ''slip'' microscale boundary condition cited in Ref. [41] for possible circumstances wherein $D_{\parallel}\neq 0$ at the wall, and hence for which the zero flux specification, Eq. (20), would result in a nonexistent solution). Despite the fact that Eq. (21) is not a boundary condition, but is rather a condition at a boundary, we will nevertheless continue to refer to the condition (21) [or, equivalently, (20)] in what follows as a ''boundary condition.'' This is done in the spirit of the claim of the molecular dynamic simulations [3,7]. Subsequently, we will demonstrate, contrary to this claim, that the *macroscale* flux density, $\mathbf{J}^0$, say, entering into the conventional macroscale Fick's law continuum diffusion equation, $\nabla^2 P=0$, does not vanish at the wall, $y=0$, despite the vanishing of the exact *microscale* flux density $\mathbf{J}$ at the wall.

Attention is limited in what follows to physical circumstances wherein both $\epsilon \ll 1$ and $\delta \ll 1$. The issue thereby engendered, namely, of the relative magnitude of the ratio $\epsilon/\delta \equiv a/l$, entails three possible scenarios: $\epsilon/\delta \ll 1$; $\epsilon/\delta \gg 1$; and $\epsilon/\delta \sim O(1)$. It will be assumed in the subsequent analysis that the last condition prevails. This choice is dictated exclusively by considerations of simplicity of analysis. Adoption of the first or second choices would have required us to perform two singular perturbation analyses, rather than one, in a sequential manner so as to take account of the existence of *three* different length scales, namely, a, l, and L, in the analysis [45,46]. However, final results and conclusions for the three different situations are almost identical as regards the L-scale outer solution (the *f-f* domain of interest to continuum mechanicians), whence for illustrative purposes we consider only the indicated case. Furthermore, having supposed that $\epsilon/\delta \sim O(1)$, we may henceforth assume without loss of generality that $\delta=\epsilon$, since any $O(1)$ distinctions between the two parameters may be absorbed into the precise definition of the molecular length scale l.

C. Exact, outer (continuum-mechanical), and inner (molecular simulation) scales

The set of exact, $(l \oplus L)$-scale equations (17)–(20) [or Eq. (21)], which explicitly incorporate both physicochemical (potential-energy) and mechanical (steric hydrodynamic) wall effects, can be shown to possess a solution which both exists and is unique, based jointly upon (i) the prescribed boundary conditions; (ii) the constitutive forms assumed for the fields appearing in these equations; and (iii) specification of the y dependence of the phenomenological coefficients appearing in the latter constitutive equations. The corresponding probability density field $P(x,y;\delta)$ obtained as their solution then constitutes an ''exact'' physical description of the diffusion scenario in the sense that P embodies both *f-f* and *s-f* forces throughout the entire fluid domain, and at all length scales. It is notable that this microscale physical description, together with the explicit microscale phenomenological diffusivity data required therein, supports the contention that $\mathbf{J}=\mathbf{0}$ at the wall, the claim of the molecular simulations [3].

However, a conventional macroscale Fick's law formulation of the above two-dimensional problem for P would entail a force-free constitutive expression, characterized by a position-independent diffusivity $(D_\infty=1)$. The informal intuitive ''derivation'' of this conventional formulation from Eqs. (17)–(19), given below, involves introducing the naive assumption that, simply because $\delta=\epsilon \ll 1$, one may thereby *a priori* set $\delta=\epsilon=0$ in Eqs. (17) and (19), whereupon for all $y>0$ one would have that $D_{\parallel}(\infty)=D_{\perp}(\infty)=D_\infty$. [Implicit in this replacement of δ and ϵ by their limiting values is the fundamentally incorrect assumption that the field $P(x,y;\delta)$ possesses a regular, rather than singular, perturbation expansion in the small parameter $\delta=\epsilon$.]

Upon denoting this zero-order approximate solution by $P^0(x,y)$, such a simplification yields, with y lying in the range $0<y<\infty$,

$$D_\infty\left(\frac{\partial^2 P^0}{\partial x^2}+\frac{\partial^2 P^0}{\partial y^2}\right)=0, \tag{22}$$

along with the following pair of boundary conditions imposed at the ends of the cell:

$$P^0(x=0,y)=P_1; \quad P^0(x=1,y)=P_2, \tag{23}$$

together with

$$D_\infty\frac{\partial P^0}{\partial y}=0 \quad \text{at } y=0. \tag{24}$$

Were we in the same naive spirit displayed above to set $\epsilon=0$ in the ''boundary condition'' (21), this would further require that

$$D_\infty\frac{\partial P^0}{\partial x}=0 \quad \text{at } y=0 \Rightarrow \left.\frac{\partial P^0}{\partial x}\right|_{y=0}=0 \quad \forall(0<x<1), \tag{25}$$

since $D_\infty=1$ is a nonzero constant. However, the solute reservoir boundary conditions at $x=0$ and $x=1$ imposed upon the field P^0 via Eq. (23) for all $\infty>y>0$ invalidate the possibility that $(\partial P^0/\partial x)_{y=0}=0$ for all x unless the field is singular at $y=0$. Consequently, stipulating that $\mathbf{J}^0=\mathbf{0}$ at $y=0$ as a requirement demanded of the solution P^0 of the macroscale diffusion equation (22) leads to an inconsistency, despite the fact that the exact condition $\mathbf{J}=\mathbf{0}$ at $y=0$ is consistent with the exact microscale diffusion equation (17).

This paradox, stemming from an irreconcilable incompatibility existing between the differential equations and requisite boundary conditions, is inherent to the class of problems involving a singular layer, the latter arising from the presence of a small length-scale parameter (quantified in our problem by $\delta=\epsilon\ll 1$). Resolution of this paradox requires a detailed examination of the near-wall boundary layer region, $y/\delta\sim O(1)$, where our naive assumption of setting $\delta=\epsilon=0$, $D_\parallel(y)=D_\perp(y)=D_\infty=1$, and $E(y)=E_\infty=\text{const}$ results in a fundamental inconsistency. This region constitutes the inner region, whose solution determines the ''boundary condition'' (more properly, the matching condition) imposed on the outer regime at the wall, $y=0$. In the next section we undertake a detailed analysis of this inner layer.

For later reference we note that the solution of the intuitive trio of equations (22)–(24), corresponding to the classical Fick's law continuum-mechanical formulation $\nabla^2 P^0=0$, is

$$P^0(x)=P_1-(P_1-P_2)x, \tag{26}$$

along with the following expressions for the flux components:

$$J_x^0=D_\infty(P_1-P_2)=\text{const}\neq 0, \quad J_y^0=0. \tag{27}$$

As already observed, the first member of the latter equation does not satisfy Eq. (21); consequently, Eq. (20) is violated by this approximate solution. The conventional Fick's law solution (26) and (27) will be shown in what follows to correspond formally to the zero-order outer field, obtained by the following limiting procedure applied to the exact field P:

$$P^0 \overset{\text{def}}{=} \lim_{\substack{\delta\to 0\\ y\ \text{fixed}}} P(x,y;\delta). \tag{28}$$

The preceding macroscale field P^0 does not explicitly account for wall effects [cf. Eqs. (26), (6), and (17) under the limiting operation of Eq. (28)]. Rather, as will be subsequently outlined, such wall effects are embodied either by an *effective* macroscale boundary condition or, in the case of solute adsorption, by a macroscale *surface-excess* areal density field ascribed to the wall.

As earlier observed, molecular dynamic simulations are currently capable of probing only the region $y=O(\delta)$ very near to the wall, wherein molecular wall effects are significant. This contrasts with the above circumstances involving the classical continuum field P^0, wherein such *s-f* wall effects are wholly absent. As such, conventional *l*-scale molecular dynamic simulations cannot and do not embody classical continuum *L*-scale attributes of the type described above, since such attributes reflect the absence of wall effects, and hence represent valid descriptions of the physics only in the far-field outer region $y=O(1)$. The ''simulation-like'' region $y=O(\delta)$ is known as an inner region in the generic terminology of singular perturbation analysis [23–28]. The corresponding inner field, quantifying the attributes of the exact field in this region, can thereby be envisioned as deriving from the exact field equations (17)–(20) via the following limiting process:

$$\tilde{P}^0 \overset{\text{def}}{=} \lim_{\substack{\delta\to 0\\ \tilde{y}\ \text{fixed}}} P(x,\tilde{y};\delta), \tag{29}$$

in which the stretched, boundary layer variable

$$\tilde{y} \overset{\text{def}}{=} \frac{y}{\delta} \tag{30}$$

represents the inner independent variable.

A uniformly valid asymptotic representation of the exact $(l\oplus L)$-scale field P, the latter satisfying the exact equations (17)–(20), accurate to the first order in δ may be obtained by a composite joining of the respective inner and outer fields by invoking appropriate asymptotic matching conditions—thereby ensuring a smooth transition between the simulation-like *l*-scale inner field and the classical *L*-scale macrocontinuum outer field. In Fig. 3 we highlight these fields in relation to the exact $(l\oplus L)$-scale microcontinuum field by delineating the regions wherein each represents a locally valid description of the exact physics.

In what follows, we elucidate the above physical description by explicitly identifying the inner and outer equations quantifying the inner and outer fields, as well as the boundary conditions to be satisfied by each of these two fields. It

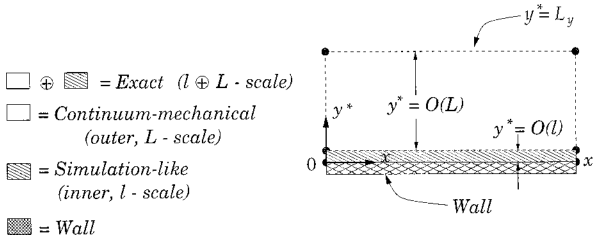

FIG. 3. Illustration of the respective physical (i.e., dimensional) domains of the exact $(l\oplus L)$-scale fields, the outer (continuum-mechanical) L-scale fields, and the inner (simulation-scale) l-scale fields.

will be seen that the equation governing the outer (zero-order) field P^0 formally reduces to the classical Fick's law diffusion equation $\nabla^2 P^0(x,y)=0$, which is to be solved subject to the two end reservoir boundary conditions, and which automatically satisfies the zero-normal-flux condition at the wall by virtue of its one-dimensional character. The corresponding inner (zero-order) field $\tilde{P}^0$ will be chosen, *inter alia*, such as to satisfy Eq. (20), thereby assuring the consistency of the governing equations with the boundary conditions. The exact solution (or, more properly, the composite zero-order solution), obtained by appropriately combining these two fields, will be shown to be identical to the outer solution, except for a thin boundary layer region very near to the wall. This singular perturbation analysis, outlined below, illustrates the situation wherein the detailed analysis of the inner region serves to provide the effective macroscale boundary condition to be imposed at the wall $y=0$. In a subsequent section we use identical concepts to illustrate a different scenario, involving so-called ''adsorption'' phenomena, wherein the potential-energy contribution to the *s-f* wall effects is implicitly manifested in the outer-scale equations via the additional presence of L-scale ''surface-excess'' fields.

D. Outer equations

Based upon the scaling arguments explicit and implicit in the arguments of the exact governing equations (17)–(20) we assume, subject to *a posteriori* verification, that for $\delta\ll 1$ the solution of this exactly posed system of equations possesses the following *regular* perturbation expansion:

$$P(x,y;\delta)=P^0(x,y)+\delta P^1(x,y)+\delta^2 P^2(x,y)+\cdots, \tag{31}$$

together with comparable expansions for $J_x(x,y;\delta)$ and $J_y(x,y;\delta)$. The intuitive arguments for small δ, presented in connection with the approximate solution appearing in Eqs. (26)–(27), suggest that the expansion (31) will, in general, be nonuniformly valid. In particular, it is expected to be applicable only in the region $y\gg\delta$, far from the wall. The leading term $P^0(x,y)$ of the above expansion corresponds to the field defined in Eq. (28). While we allow in Eq. (31) for the fact that the leading term may depend upon y, it will, in fact, prove to be independent of y, and hence be functionally dependent only upon x, as in Eq. (26).

Upon substituting Eq. (31) into the exact microscale equations (17) and (18), and equating terms of equal order in δ in the resulting expressions, we find that the leading-order field obeys the intuitively derived equations already set forth in (22) and (23). We have not, however, substituted the expansion (31) into the exact microscale wall boundary conditions (19) and (21) since we do not expect the outer expansion (31) to be valid within the boundary layer region $y=O(\delta)$ existing near the wall. In the absence of such wall boundary conditions the solution of the zero-order outer equations (22) and (23) is not unique. As will be shown, the solution of the latter equations is rendered unique by imposing a matching condition between the outer expansion (31) and the inner expansion [cf. Eq. (38)] [47].

E. Inner equations

In order to establish the inner equations we need to rescale the y coordinate by stretching it, as indicated in Eq. (30). Insertion of this definition of $\tilde{y}$ into the exact microscale transport equation (17) yields

$$\delta^2 D_\parallel(\tilde{y})\frac{\partial^2 P}{\partial x^2}+\frac{\partial}{\partial\tilde{y}}\left[D_\perp(\tilde{y})\left(\frac{\partial P}{\partial\tilde{y}}+P\frac{dE(\tilde{y})}{d\tilde{y}}\right)\right]=0. \tag{32}$$

The latter constitutes a reformulation of the original, exactly posed microscale problem governing the concentration field $P\equiv P(x,\tilde{y};\delta)$, albeit now expressed in terms of inner variables. The functional forms of the exact flux components can similarly be expressed in terms of the inner independent variable as

$$J_x=-D_\parallel(\tilde{y})\frac{\partial P}{\partial x} \tag{33}$$

and

$$J_{\tilde{y}}=-\frac{D_\perp(\tilde{y})}{\delta}\left(\frac{\partial P}{\partial\tilde{y}}+P\frac{dE(\tilde{y})}{d\tilde{y}}\right). \tag{34}$$

To render the functional dependencies of P and the flux components J_x and $J_{\tilde{y}}$ explicit, we make use of the following choice of scaled *dependent* variables:

$$\tilde{P}(x,\tilde{y};\delta)\overset{\text{def}}{=}P(x,y=\delta\tilde{y};\delta), \tag{35}$$

$$\tilde{J}_x(x,\tilde{y};\delta)\overset{\text{def}}{=}J_x(x,y=\delta\tilde{y};\delta), \tag{36}$$

and

$$\tilde{J}_{\tilde{y}}(x,\tilde{y};\delta)\overset{\text{def}}{=}\frac{1}{\delta}J_y(x,y=\delta\tilde{y};\delta). \tag{37}$$

We assume, subject to *a posteriori* verification, that for $\delta\ll 1$ the solution of the exact microscale equation (32) can be expressed as a perturbation series of the form

$$\tilde{P}(x,\tilde{y};\delta)=\tilde{P}^0(x,\tilde{y})+\delta^2\tilde{P}^1(x,\tilde{y})+\delta^4\tilde{P}^2(x,\tilde{y})+\cdots. \tag{38}$$

Furthermore, to ensure consistency with the above expansion, the corresponding flux components $\tilde{J}_x$ and $\tilde{J}_{\tilde{y}}$ also need to be expressed as perturbation expansions of the forms

$$\tilde{J}_x(x,\tilde{y};\delta)=\tilde{J}_x^0(x,\tilde{y})+\delta^2\tilde{J}_x^1(x,\tilde{y})+\delta^4\tilde{J}_x^2(x,\tilde{y})+\cdots \quad (39)$$

and

$$\tilde{J}_{\tilde{y}}(x,\tilde{y};\delta)=\tilde{J}_{\tilde{y}}^0(x,\tilde{y})+\delta^2\tilde{J}_{\tilde{y}}^1(x,\tilde{y})+\delta^4\tilde{J}_{\tilde{y}}^2(x,\tilde{y})+\cdots. \quad (40)$$

Attention is restricted in the remainder of this subsection to the equations and boundary conditions governing the zeroth-order inner fields $\tilde{P}^0$, $\tilde{J}_x^0$, and $\tilde{J}_{\tilde{y}}^0$. Based upon the assumed functional form (38) of the perturbation series we can formally define the zeroth-order inner probability density field as already set forth in Eq. (29). Upon utilizing the exact microscale constitutive equation (3) together with the scaling embodied in Eqs. (35)–(37), the functional forms of the leading-order flux components can be expressed as

$$\tilde{J}_x^0=-D_\parallel(\tilde{y})\,\frac{\partial\tilde{P}^0}{\partial x} \quad (41)$$

and

$$\tilde{J}_{\tilde{y}}^0=-D_\perp(\tilde{y})\left(\frac{\partial\tilde{P}^0}{\partial\tilde{y}}+\tilde{P}^0\frac{dE(\tilde{y})}{d\tilde{y}}\right). \quad (42)$$

As previously indicated in Ref. [41], the diffusivity components $D_\parallel(\tilde{y})$ and $D_\perp(\tilde{y})$ possess the following limiting properties:

$$D_\parallel(\tilde{y}) \text{ and } D_\perp(\tilde{y})\to 0 \quad \text{as } \tilde{y}\to 0. \quad (43)$$

The explicit functional forms of these components need not be invoked, however, in the analysis that follows.

Substitution of the inner expansions (38)–(40) into both the exact equations (32)–(34) and the exact wall boundary conditions (19) and (21) enables the extraction of those equations and boundary conditions that are mutually compatible at a particular order of expansion. In particular, the diffusion equation governing the zeroth-order inner field can be identified as

$$\frac{\partial}{\partial\tilde{y}}\left[D_\perp(\tilde{y})\left(\frac{\partial\tilde{P}^0}{\partial\tilde{y}}+\tilde{P}^0\frac{dE(\tilde{y})}{d\tilde{y}}\right)\right]=0, \quad (44)$$

which is to be solved subject to the zero-order inner wall boundary conditions

$$\tilde{J}_x^0=0 \quad \text{at } \tilde{y}=0 \quad (\forall x) \quad (45)$$

and

$$\tilde{J}_{\tilde{y}}^0=0 \quad \text{at } \tilde{y}=0 \quad (\forall x). \quad (46)$$

Had we substituted the inner expansion (38) into the two end boundary conditions (18), the field $\tilde{P}^0$ would have been required to satisfy the pair of boundary conditions

$$\tilde{P}^0(x=0,\tilde{y})=P_1=\text{const} \quad (\forall\tilde{y}) \quad (47)$$

and

$$\tilde{P}^0(x=1,\tilde{y})=P_2=\text{const} \quad (\forall\tilde{y}). \quad (48)$$

However, since the inner expansion is not expected to be valid for all $\tilde{y}$, but rather only for $\tilde{y}=O(1)$, satisfaction of these two boundary conditions is not required of the inner field.

A first integral of Eq. (44) is

$$D_\perp(\tilde{y})\left(\frac{\partial\tilde{P}^0}{\partial\tilde{y}}+\tilde{P}^0\frac{dE(\tilde{y})}{d\tilde{y}}\right)=\alpha(x), \quad (49)$$

whence from Eq. (42) it follows that

$$\tilde{J}_{\tilde{y}}^0(x,\tilde{y})=-\alpha(x) \quad (\forall\tilde{y}). \quad (50)$$

The vanishing normal flux boundary condition (46) requires that $\alpha(x)=0$. Consequently, Eq. (49) becomes

$$\frac{\partial\tilde{P}^0}{\partial\tilde{y}}+\tilde{P}^0\frac{dE(\tilde{y})}{d\tilde{y}}=0, \quad (51)$$

the solution of which can be expressed as

$$\tilde{P}^0(x,\tilde{y})=\beta(x)\exp[-E(\tilde{y})], \quad (52)$$

with $\beta(x)$ an integration function.

Introduction of this last equation into Eq. (41) yields

$$\tilde{J}_x^0(x,\tilde{y})=-D_\parallel(\tilde{y})\,\frac{d\beta(x)}{dx}\exp[-E(\tilde{y})]. \quad (53)$$

The boundary condition (45) imposed on the parallel flux component $\tilde{J}_x^0$ is automatically satisfied for any choice of $\beta(x)$ by virtue of Eq. (43), positing the vanishing of the parallel diffusivity component at the wall. Equation (52) thus satisfies the governing zero-order inner diffusion equation (44) as well as the corresponding parallel and normal flux conditions (45) and (46) at the wall. However, consistent with our remarks following Eqs. (47) and (48), the solution (52) is incapable of satisfying the pair of prescribed end boundary conditions (47) and (48) for *all* $\tilde{y}$. We note, however, for $\tilde{y}\to\infty$ (strictly, for $\tilde{y}\gg\delta$), that

$$E(\tilde{y})\to E_\infty=\text{const} \quad (54)$$

[cf. Eq. (1)], whereupon Eq. (52) adopts the asymptotic form

$$\tilde{P}^0(x,\tilde{y}\gg\delta)\cong\exp(-E_\infty)\beta(x). \quad (55)$$

F. Matching conditions

The inner and outer solutions $\tilde{P}$ and P need to be matched in their common domain of validity. This requires that the inner and outer expansions of the exact solution of the original problem posed by Eqs. (17)–(20) be asymptotically equal in the intermediate region $y=O(\delta^q)$ $(0<q<1)$ lying between the outer region $y=O(1)$, corresponding to $q=0$, and the inner region $y=O(\delta)$, corresponding to $q=1$. To terms of zero order in the respective expansions, this matching condition requires that, loosely speaking [23–28],

$$P^0(x,y\to 0)\cong\tilde{P}^0(x,\tilde{y}\to\infty). \quad (56)$$

Upon invoking Eq. (55) this necessitates that the outer solution asymptotically adopt the form

$$P^0(x,y\rightarrow 0)\cong \exp(-E_\infty)\beta(x). \tag{57}$$

The only solution of the zero-order outer equation (22) and corresponding pair of boundary conditions (23) that is compatible with the asymptotic functional form (57) is the y-independent solution,

$$P^0(x)=P_1-(P_1-P_2)x, \tag{58}$$

already derived in Eq. (26) by invoking intuitive arguments for the case $\delta \ll 1$. From Eq. (57), the latter is equivalent to the choice

$$\beta(x)=\exp(E_\infty)[P_1-(P_1-P_2)x]. \tag{59}$$

Substitution of the preceding expression into Eq. (52) yields

$$\tilde{P}^0(x,\tilde{y})=[P_1-(P_1-P_2)x]\exp[E_\infty - E(\tilde{y})], \tag{60}$$

constituting the complete and unique solution for the zeroth-order inner concentration field. In the usual manner of matched asymptotic schemes [23–28] the outer and inner fields, Eqs. (58) and (60), can be appropriately combined so as to furnish a uniformly valid solution of the exact field $P(x,y;\delta)$ for circumstances wherein $\delta \ll 1$:

$$P(x,y;\delta)=[P_1-(P_1-P_2)x]\exp[E_\infty - E(\delta y)]+O(\delta). \tag{61}$$

Proceeding as in Eq. (56), but with J_y now written in place of P, we find with the help of Eq. (50) [in which $\alpha(x)=0$] that J_y^0 is required to satisfy the matching condition $J_y^0(x,y\rightarrow 0)=0$. Consequently, the normal flux component at the wall is required to satisfy the following zero-order outer, macroscale ''boundary condition:''

$$J_y^0(x,y=0)\equiv -D_\infty \frac{\partial P^0(x,y=0)}{\partial y}=0. \tag{62}$$

This result constitutes one of the central results of this section. That is, by employing rigorous singular perturbation techniques we have proved that the boundary condition satisfied by the macroscale concentration field requires that only the normal flux component vanish at the wall, this despite the fact that the corresponding *microscale* field trivially possesses the property that both the normal and the tangential flux components vanish at the wall [48].

G. Discussion

Using a formal singular perturbation scheme we have illustrated in this section the manner whereby a consistent perturbation solution of the exactly posed microscale problem, defined jointly by the differential equation (17) and conditions (18)–(20) at the boundaries, can be obtained. It is pertinent here to recount the major steps in that analysis, so as to highlight the salient features of the argument. Initially we formulated a complete microscale continuum description of the ''exact'' $(l\oplus L)$-scale physics quantifying the problem of Brownian diffusion in a binary fluid system, embodying *s-f* effects arising from wall-fluid interactions. The length scale characterizing this microscale formulation was specifically chosen so as to correspond to the scale of molecular simulations, wherein wall interaction effects are taken into account. Moreover, the ''conditions at the boundary'' satisfied by this microscale description were shown from hydrodynamic mobility considerations to correspond trivially to the vector no-flux condition $\mathbf{J}=\mathbf{0}$ at the wall—the generic claim of the molecular dynamic simulation calculations [3] in binary fluid transport systems [49]. Thus, the ''exact'' flux boundary condition, requiring that $\mathbf{J}=\mathbf{0}$ at the wall (or, equivalently, that the individual species velocities vanish at the wall), needs to be applied to the system of equations written at this microscale.

In order to make an explicit connection with the conventional macroscale Fick's law formulation of this elementary diffusion problem, we adopted a naive (outer scale) viewpoint, wherein all the small nondimensional parameters appearing in the exact microscale equations were set equal to zero at the outset of the analysis. This yielded the familiar Fick's law diffusion equation (characterized by a position-independent diffusivity). We then pointed out that any effort to apply at this scale the literal wall boundary conditions, valid at the ''inner'' or ''simulation'' scale, would lead to an inconsistency with the other boundary conditions, namely, those imposed within the reservoirs situated at the two ends of the diffusion cell. This then suggested the existence of a singular layer near the wall, where the conventional continuum-mechanical Fick's law formulation is invalid, and hence needs to be refined so as to admit the simulation-scale vanishing vector flux boundary condition $\mathbf{J}=\mathbf{0}$ at the ''wall'' (i.e., at the planar surface $y^*=a$ situated at a distance from the actual wall equal to the radius of a Brownian solute molecule). We then effected a singular perturbation analysis to show how a solution consistent with all of the simulation-scale conditions prevailing at the boundaries may be obtained. The vanishing-normal-flux ''boundary condition'' at the wall [equivalent to $\mathbf{n}\cdot\mathbf{J}^0(y=0)=0$, with $\mathbf{n}$ the unit vector normal to the wall; cf. Eq. (62)], imposed on the macroscale continuum-mechanical equations, was derived by matching the outer and inner solutions, each of which was heretofore separately nonunique. This allowed us to propose a uniformly valid composite solution, one which coincided with the classical one-dimensional linear concentration profile almost everywhere within the diffusion cell except near the wall, while simultaneously matching the two-dimensional inner solution in a region of thickness $O(\delta)$ proximate to the wall. This inner solution, which embodied the wall effects explicitly present in the exact microscale description (but lacking in the macroscale description), allowed for satisfying the $\mathbf{J}=\mathbf{0}$ boundary condition at the wall.

The preceding analysis of this elementary diffusion problem forcefully underlines our main criticisms [6] of the indiscriminate use of molecular simulations to discern the boundary conditions applicable to conventional continuum equations, the latter referring to those continuum equations that embody *f-f* forces but not *s-f* forces. As discussed above, a microscale continuum equation was required to satisfy the additional tangential flux boundary condition arising from the short-range wall effects. However, this new boundary condition and the accompanying refined equation explicitly embodying this flux condition did not impact significantly on the well-known solution of the classical Fick's law one-dimensional diffusion solution for the solute concentration field, except in a thin boundary layer of thickness $O(\delta) \times(\delta=l/L \ll 1)$ proximate to the wall. Furthermore, the boundary conditions that one must impose on this outer macroscale Fick's law diffusion equation in order that it properly capture the residual long-range effects of the detailed wall physics were derived as being the outer limits of the solutions of the inner equations, rather than by directly imposing the literal boundary conditions demanded of the inner equations—the latter corresponding to those discerned by molecular simulations.

In the spirit of simplicity accompanying this article we excluded the effects of wall roughness. The presence of such geometric asparities, superposed on the otherwise perfectly smooth surface envisioned in the analysis, introduces yet another length scale into the problem. In most physical circumstances this scale can be expected to be small compared with the apparatus length scale L. On the other hand, the length scale of the roughness—say l_r, the *mesoscale*—will generally be significantly greater than that of the molecular wall forces, as well as of the size of the Brownian molecules, resulting in the dual inequality $L \gg l_r \gg l$. In such circumstances the preceding type of singular perturbation analysis, whereby we derived the zero-normal-flux macroscale boundary condition at the wall, can again be invoked, beginning at the microscale Brownian molecule level, to furnish the comparable mesoscale boundary conditions on the rough wall. Explicitly, at each such ''mesoscale point'' lying on the rough surface one would almost certainly find as the formal result of such an analysis that $\mathbf{n}\cdot\mathbf{J}=0$ [whereas $(\mathbf{I}-\mathbf{nn})\cdot\mathbf{J}\neq\mathbf{0}$], with $\mathbf{n}$ the unit normal vector at a point on the rough surface, and $\mathbf{J}$ the mesoscale flux density. These would then constitute mesoscale boundary conditions to be imposed on the new inner mesoscale equations, the latter now being written at the length scale l_r of the roughness. The outer equations (applicable at the Fick's law macroscale level, where the roughness is not observable, and hence the l_r-scale rough boundary appears as a smooth L-scale wall), together with the requisite mesoscale/macroscale matching conditions, can be determined by effecting a similar singular perturbation analysis at the scale of the roughness elements. This general procedure was employed in a seminal paper by Richardson [31] (see also Jansons [50]) to illustrate the robustness of the classical no-slip, fluid-mechanical, mass-average velocity boundary condition governing the flow of homogeneous fluids relative to solid walls [51].

In the next section we further elaborate our criticism of the failure of some simulations to give cognizance to the physical distinction existing between ''inner'' and ''outer'' limits as $l/L \rightarrow 0$. In particular, we address the phenomenon of continuum surface adsorption [52], a condition that has no counterpart at the corresponding molecular scale. The main point to be addressed is the fact that the magnitudes of the potential-energy forces used in the simulations generally fail to distinguish ''adsorptive'' *s-f* molecular forces (which act disproportionately on one of the two species) from ''democratic,'' nonadsorptive *s-f* molecular forces (which act more or less equally on both species) by virtue of the fact that such simulations ignore the macroscopic length scale L of the physical apparatus within which the adsorption occurs.

In the analysis that follows we briefly detail the manner whereby one supplements the continuum-scale transport equations, corresponding to the conventional Fick's law diffusion equation governing the bulk volumetric density solute concentration field, with a comparable L-scale Fick's law *surface diffusion* equation governing the surface areal density solute concentration field. The macroscale areal surface concentration p and lineal flux density vector $\mathbf{j}$ fields appearing in the latter refer to idealizations arising from a lack of resolution of the molecular-scale phenomena occurring near to the wall. While literal ''surface'' transport effects can indeed be discerned from molecular simulations, continuum-scale surface transport phenomena cannot be directly discerned by simply investigating the motion of those molecules proximate to the walls. Rather, their identification and quantification requires that one explicitly address the existence of the apparatus length scale L.

III. SURFACE ADSORPTION AND TRANSPORT

Here, we extend the analysis of Sec. II so as to inject additional issues relating to the adsorption and subsequent surface transport of the Brownian solute molecules. While the equilibrium adsorption aspects of these classical phenomena are generally quite well understood at both the macroscopic and molecular levels, the same cannot be said of the nonequilibrium surface transport properties. This fact provides the motivation for the ensuing analysis, namely, to clarify the strictly continuum-mechanical nature of the surface transport process by drawing a sharp distinction with the strictly local molecular view of the phenomenon. In this context it will be shown that the concepts of surface adsorption and transport are devoid of meaning on the length scale at which molecular wall-fluid interaction effects are resolvable [53]. Rather, these concepts arise at the next scale of resolution, corresponding to the outer scale of our equations, where such wall-interaction effects are implicitly included in the boundary conditions or, as argued below, equivalently in the auxiliary surface areal density transport fields serving to supplement classical, bulk volumetric density transport fields; that is, the L-scale surface fields serve the role of boundary conditions imposed upon the conventional L-scale Fick's law volumetric fields [cf. Eq. (85)]. As such, molecular-level simulations cannot discern these continuum-scale surface concepts unless they are also attuned to probing the coarse-grained macrocontinuum scale. In lieu of formal singular perturbation techniques, for simplicity's sake in the following analysis we adopt intuitive ''pillbox''-type arguments (cf. Refs. [52,54] for closely related applications utilizing pillbox arguments), to derive the continuum-scale equations accompanying the phenomena of surface adsorption and diffusion. It is a straightforward, albeit lengthy, matter to prove that rigorous singular perturbation arguments furnish boundary conditions (imposed upon the leading-order perturbation fields) that are identical to those derived via the informal pillbox arguments which follow below. References [46,55,56,57] use such perturbation schemes to address similar issues relating to *liquid-liquid* interfaces. The case of *transient* adsorption at a solid wall is likewise treated rigorously by Shapiro, Brenner, and Guell [58] in the context of aerosol and hydrosol deposition on surfaces.

The surface transport equation eventually derived in this section [cf. Eq. (81) or (82)] contradicts the boundary condition $\mathbf{n}\cdot\mathbf{J}^0(x,y=0)=0$ derived in the previous section. This disparity reflects the difference in the specific natures of the respective wall-interaction potential forces acting on each of the two diffusing species. Adsorption forces require an attractive potential well (refer to Fig. 2), wherein the condition $\delta\exp(-E_m)\ll 1$ would fail, with E_m the potential-energy minimum (see the caption of Fig. 2 for a more precise distinction between the adsorptive and nonadsorptive cases). In turn, this would require us to modify our straightforward singular perturbation approach in order to account for this new feature. Subtleties accompanying the various forms exhibited by potential wells are detailed by Shapiro, Brenner, and Guell [58] and will not be repeated here. Indeed, rather than attempting to present a comprehensive treatment of surface adsorption phenomena, our main objective in this section is to illustrate, in as elementary a fashion as possible, the physical origin of surface concentration and flux fields, in addition to quantifying their transport. Thus, we distinguish between the results of the previous section and those to be derived in the present section as arising from the different forms of the interaction potential in the two cases, while eschewing detailed considerations emanating from these distracting subtleties.

A. Surface concentration

Pillbox-type analyses are performed by examining at both the outer and exact scales the total amounts of solute (and other extensive continuum fields) identified at each scale as being contained within a rectangular pillbox surmounting the lower wall $y^*=0$ and extending to the midplane between the two walls, and subsequently assigning the difference between the two amounts to a continuum-mechanical surface(-excess) areal density field defined at the macroscale. This scheme, which at the macroscale views the solute as being distributed between a bulk (volumetric) phase and a surface (areal) or absorbed phase, serves to assure consistency of the total amount of the solute (or other extensive entity) present within the system, whether viewed at the macroscale L or the exact scale $l\oplus L$.

Contrary to what is often assumed to be the case, surface concentration does not refer literally to the exact areal concentration (i.e., solute mass or number of molecules per unit area) of the solute ''adsorbed'' at the wall. Rather, this concept—which is more appropriately termed surface-excess concentration—arises from the need to incorporate the differences, described above, existing between the coarse-grained bulk concentration field (representing the leading-order outer, or macroscale concentration field) and the exact concentration field incorporating the wall effects (i.e., the leading-order composite solution of the singular perturbation analysis). In Sec. II we saw that wall effects, as embodied in the wall-interaction potential, lead to a modification of the outer solution near the wall, thereby yielding the following zero-order inner concentration distribution:

$$\tilde{P}^0(x,y=\delta\tilde{y})=P^0(x,y=0)\exp[E_\infty-E(\tilde{y})]. \tag{63}$$

The uniformly valid composite solution thereby obtained is

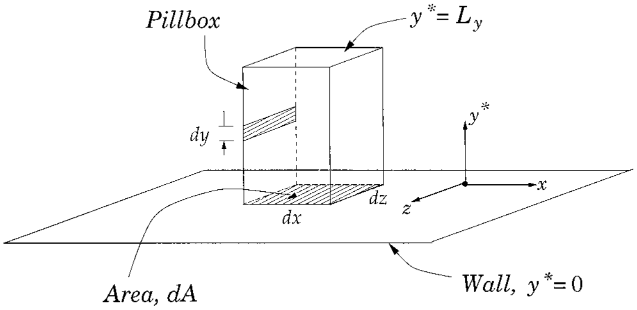

FIG. 4. Differential rectangular parallelepipedal pillbox of differential cross-sectional area $dA=dx\,dz$, differential volume $dV=dA\,dy$, and finite (dimensional) height $y^*=L_y$ above the wall [the latter corresponding to a nondimensional height of $y=(L_y-a)/L_y\equiv 1-\epsilon$].

$$P(x,y;\delta)=P^0(x,y)+P^0(x,y=0)\times\{\exp[E_\infty-E(\tilde{y})]-1\}+O(\delta). \tag{64}$$

It is easily verified that the latter solution asymptotically matches the inner and outer solute concentration and flux fields in the intermediate, overlap region. Equation (64) constitutes the exact solution of the problem, correct to the zeroth order in δ.

Consider the differential rectangular parallelepipedal pillbox illustrated in Fig. 4 of infinitesimal cross-sectional area $dA=dx\,dz$ and finite height, the latter extending from the lower wall to the midplane between the two walls in our example. In terms of our current dimensionless variables, whose length scaling is based on the half-gap width $L_y\equiv L$, the pillbox posseses a physical height $y^*=L_y$, so that, nondimensionally, $y=1-\epsilon$ at the upper surface of the pillbox. Viewed at a coarse-grained outer scale, the number of solute molecules dW^0 *apparently* contained within the pillbox is

$$dW^0=dA\int_0^{1-\epsilon}dy\,P^0(x,y), \tag{65}$$

whereas at the exact scale the corresponding solute number is

$$dW=dA\int_0^{1-\epsilon}dy\,P(x,y;\delta). \tag{66}$$

Therefore, to assure quantitative consistency between the numbers of solute molecules recorded at both the outer and exact scales, the difference

$$dW^s\overset{\text{def}}{=}dW-dW^0 \tag{67}$$

in the numbers of solute molecules contained within the pillbox volume is assigned to that portion of the surface represented by the area *dA*. This leads one to define the surface (-excess) areal solute number density concentration field:

$$p(x)\overset{\text{def}}{=}\lim_{\delta\to 0}\frac{dW^s}{dA}\equiv\lim_{\delta\to 0}\int_0^{1-\epsilon}dy[P(x,y;\delta)-P^0(x,y)]. \tag{68}$$

The coarse-scale continuum field $p(x)$ is loosely interpreted as representing the number of adsorbed solute molecules per unit area at the point (x, z) on the wall $y=0$, although, of course, it represents the *excess* number. Upon introducing Eq. (64) into Eq. (68) we obtain

$$p(x)=HP^0(x,y=0),$$

$$\mathrm{H}=\delta 0\infty\ \mathrm{dy}\{\mathrm{exp}[E\infty-E(y)]-1\}=\mathrm{const.} \tag{69}$$

Note that in the upper integration limit we have replaced $\tilde{y}=(1-\epsilon)/\delta$ by ∞ as a consequence of the smallness of the parameter δ, coupled with the fact that $\epsilon=O(\delta)$.

The last equation constitutes a Henry's law equilibrium adsorption relation (with H the Henry's law constant), linearly relating the surface(-excess) concentration field $p(x)$ to the bulk concentration field $P^0(x,y=0)$ existing at the wall. Our derivation of this relation elucidates the origin of the concept of surface concentration. In particular, it clearly demonstrates that the notions of adsorption and surface concentration arise not from the literal presence of molecules (Brownian particles) affixed to, or even in proximity to, the surface in an *absolute* sense (i.e., independently of L), but only in a *relative* sense [59]. Explicitly, such surface concepts are attributable to the very different physical data implicitly embedded in the outer and inner fields. This example again illustrates the fundamental differences existing between the fine-scale molecular-dynamic-like viewpoint and the coarse-scale continuum-mechanical viewpoint. Explicitly, *conditions at a boundary*, as discerned by fine-scale simulations, are not to be construed as *boundary conditions* to be imposed at the macroscale. The next subsection likewise illustrates the physical origin of the similar concept of surface(-excess) diffusion.

B. Surface diffusion

Since in our model the individual Brownian solute molecules were assumed to be immobile at the wall, as implicitly stated in Eq. (20) or (21), one might naively expect the ''surface flux'' of solute to be zero, and hence surface diffusion to be absent. Indeed, were one to regard surface transport as involving the movement of molecules literally in contact with and translating along the wall, the very concept of surface diffusion would be a *non sequitur*. Despite the seeming plausibility of this vanishing-surface-flux argument, it is nevertheless invalid, a fact that is illustrated in what follows. Our basic arguments parallel those introduced in the preceding subsection in connection with the more elementary concept of surface concentration. Explicitly, what is termed ''surface transport'' originates from the difference in the net solute fluxes (parallel to the wall) through the sides of the pillbox, respectively measured at the macro- and exact scales, and subsequently assigned to the wall.

For purposes of illustration consider solute transport in the x direction through the left-hand side face of the differential pillbox portrayed in Fig. 4. Viewed at the outer scale, the time rate dN^0 of solute transport across this face in the positive x direction is given by

$$dN^0=dz\int_0^{1-\epsilon}dy\ J_x^0(x,y), \tag{70}$$

where, from Fick's law, applicable at the outer scale,

$$J_x^0(x,y)=-D_\infty\frac{\partial P^0(x,y)}{\partial x}. \tag{71}$$

In contrast, the comparable exact solute transport rate is given by

$$dN=dz\int_0^{1-\epsilon}dy\ J_x(x,y;\delta). \tag{72}$$

Analogous to the union of Eqs. (63) and (64), to terms of dominant order in δ we have the following composite expansion for the parallel solute flux component:

$$J_x(x,y;\delta)=\tilde{J}_x^0(x,\tilde{y})+J_x^0(x,y)-J_x^0(x,y=0)+O(\delta), \tag{73}$$

in which

$$\tilde{J}_x^0(x,\tilde{y})=-D_\parallel(\tilde{y})\,\frac{\partial\tilde{P}^0(x,\tilde{y})}{\partial x}. \tag{74}$$

By similar arguments to those enunciated in the preceding subsection, the difference

$$dN^s\overset{\mathrm{def}}{=}dN-dN^0 \tag{75}$$

in solute transport rates across the sidewall is assigned to the surface(-excess) lineal diffusion flux density of absorbed solute ''along the wall,'' defined as

$$j_x(x)\overset{\mathrm{def}}{=}\lim_{\delta\to 0}\frac{dN^s}{dz}\equiv\delta\int_0^\infty d\tilde{y}[\tilde{J}_x^0(x,\tilde{y})-J_x^0(x,y=0)]. \tag{76}$$

The above formula can be written in terms of the surface concentration and a phenomenological surface diffusivity as

$$j_x=-D_s\frac{dp}{dx}, \tag{77}$$

where D_s is the surface diffusivity:

$$D_s=\frac{\int_0^\infty d\tilde{y}\,D_\parallel(\tilde{y})\{\exp[E_\infty-E(\tilde{y})]-1\}}{\int_0^\infty d\tilde{y}\{\exp[E_\infty-E(\tilde{y})]-1\}}=\mathrm{const.} \tag{78}$$

The last pair of relations [60] furnish an *a priori* proof of the Fick's law–like constitutive equation for the surface diffusion flux (cf. also Ref. [52]).

The existence of both a surface diffusion flux and a surface concentration enables us to define the *surface velocity* of the solute as

$$v_x^s(x)\overset{\mathrm{def}}{=}\frac{j_x}{p(x)}. \tag{79}$$

Equivalently, from Eq. (77),

$$v_x^s(x) = -D_s \frac{d \ln p(x)}{dx} \equiv -D_s H \frac{d \ln P^0(x,y=0)}{dx}. \quad (80)$$

As earlier implied, the existence of such a surface species velocity may seem paradoxical in view of the immobility of the Brownian particles at the wall. Resolution of the apparent contradiction resides in the essential fact that surface-excess concepts, like surface concentration and surface diffusion velocity, do not depend upon the exact volumetric solute concentration or diffusion velocity fields existing at the wall $y=0$. Rather, these surface concepts are defined on the coarser outer macroscale L, wherein wall-fluid interaction effects are not explicitly present. Such interaction effects are nevertheless implicitly present, embedded in the surface areal density fields. The latter now appear as coarse L-scale fields, introduced so as to rectify the disparity existing between quantitative predictions of the extensive aspects of the pertinent fields as discerned by the macroscale and exact observers. Indeed, in the elementary problem analyzed here we have encountered no less than four different solute velocity fields v_x along the wall depending upon the scale of observation and whether or not adsorption takes place.

(i) The *exact* $(l \oplus L)$-scale solute species velocity at the wall, $v_x(x,y=0;\delta)$, which in our model was identically zero (for all δ) due to the vanishing of the parallel diffusivity component $D_\parallel$ at the wall.

(ii) The *molecular* l-scale solute particle velocity at the wall, $\tilde{v}_x^0(x,\tilde{y}=0)$, which refers to the value of the (zero-order) inner velocity at $\tilde{y}=0$. For the same reason as in (i) this velocity too was zero. It is this velocity that we identify with that calculated from molecular dynamic simulations [3].

(iii) The *bulk* L-scale solute species velocity at the wall in the absence of adsorption, $v_x^0(x,y=0)$, which refers to the value of the (zero-order) outer velocity at $y=0$ for a nonadsorptive potential-energy function. In our model this velocity is equal to $-D_\infty d \ln P^0(x,0)/dx$ which, in view of Eq. (58), is nonzero.

(iv) The *surface* L-scale solute species velocity in the presence of adsorption, $v_x^s(x)$, which arose from the definition of the surface diffusion flux so as to account for the disparity in the total amounts of solute transported parallel to the wall at the coarse-grained and exact levels of description. In our model the value of this surface velocity is given by Eq. (80) and is nonzero.

The corresponding *normal* velocity components at the wall are zero in each of the above four cases, although in the adsorption case this is true only for the special case where the reservoir concentrations P_1 and P_2 appearing in Eq. (18) are both y-independent constants. In circumstances where either is not y independent, $J_y^0(x,y=0)$ will prove to be nonzero [cf. Eq. (81) below], whence the same will prove true of the comparable solute velocity component at the wall, $v_y^0(x,y=0)$.

C. Surface transport equation

Details of the formal derivation of a (generally unsteady) surface transport equation are peripheral to the focus of this paper, and will not be presented. The expression ultimately obtained [55,57,61] is analogous to the comparable equation for fluid-fluid interfaces, and in the context of our model is given by

$$\frac{dj_x}{dx} = J_y^0(x,y=0). \quad (81)$$

This represents a special case of the (generally unsteady-state) generic flux conservation relation [57,62]

$$\frac{\partial p}{\partial t} + \nabla_s \cdot \mathbf{j} = \mathbf{J} \cdot \mathbf{n}, \quad (82)$$

where $\mathbf{n}$ points from the wall into the fluid, and $\nabla_s \overset{\text{def}}{=} (\mathbf{I} - \mathbf{nn}) \cdot \nabla$ is the surface gradient operator.

D. General macrocontinuum L-scale boundary conditions

Our analysis of the distinction between ‘‘conditions at a boundary’’ and ‘‘boundary conditions’’ was based on the particular example of the two-dimensional diffusion cell (Fig. 1)—especially the y^*-independent nature of the reservoir boundary conditions, Eqs. (13). This resulted in the classical one-dimensional y^*-independent Fick’s law solution, Eq. (26), for the macrocontinuum volumetric solute concentration field P^0 [and ultimately, in the case of adsorption, the macrocontinuum surface-excess areal solute concentration field p, given in terms of P^0 by Eq. (69)]. However, with only little additional effort it is possible to derive results for the wall boundary conditions of greater generality than those obtained for the specific example treated above. These results, which are readily obtained by employing techniques paralleling those already outlined, are briefly summarized below.

In dimensionless form, the equation governing the generally unsteady L-scale macrocontinuum field $P^0(x,y,z,t)$ is

$$\frac{\partial P^0}{\partial t} + \nabla \cdot \mathbf{J}^0 = 0, \quad (83)$$

with flux density

$$\mathbf{J}^0 = -D_\infty \nabla P^0. \quad (84)$$

The (single) scalar boundary condition imposed upon the field P^0 at a solid wall is

$$H\left(\frac{\partial P^0}{\partial t} - D_s \nabla_s^2 P^0\right) + D_\infty \mathbf{n} \cdot \nabla P^0 = 0 \quad \text{at the wall,} \quad n=0 \quad (85)$$

[cf. Eq. (82)], in which the constants H and D_s are expressed in terms of the prescribed three-dimensional phenomenological data by Eqs. (69) and (78) (wherein y appearing in those expressions is to be replaced by the distance n normal to the wall). For the nonadsorptive case, where $H=0$ (albeit to the order of our approximation in the small parameter l/L), Eq. (85) properly reduces to the nonadsorptive boundary condition,

$$\mathbf{n} \cdot \nabla P^0 = 0 \quad \text{at the wall,} \quad n=0. \quad (86)$$

In the particular example of Fig. 1, with steady-state y-independent reservoir conditions, the above equations possess the elementary one-dimensional solution cited in Eq. (26) for both the nonadsorptive and adsorptive cases.

E. Discussion

This section has served to clarify the concepts of both surface-excess adsorption and surface-excess diffusion phenomena by using a Brownian particle/plane-wall model. Explicitly, it was demonstrated that these surface notions do not possess any physical meaning at the exact and simulationlike levels of modeling. Rather, the interpretations to be ascribed to them exist only at the next coarser scale (corresponding to the outer scale in our singular perturbation analysis), wherein these fields are assigned phenomenologically to the surface so as to rectify the disparity existing between the predictions of the exact and outer volumetric density fields. Hence, simulations purporting to derive these quantities by direct probing of those molecules near to the wall will necessarily give rise to erroneous macroscale conclusions (except, possibly, in fortuitous circumstances).

IV. HYBRID COMPUTATIONS

Previous portions of this paper have attempted to elucidate a number of continuum-scale concepts, especially the molecular origin of boundary conditions and surface fields. We have consistently criticized those molecular-level simulations that claim to derive these quantities by direct probing of the discrete molecular motions occurring near the bounding walls. More explicitly, we have pointed out (i) that the physical interpretation of these notions at the continuum-mechanical scale differs fundamentally from the literal physical interpretation ascribed to them at the statistical-molecular scale; and (ii) that the fundamental differences between the two are to be explained in terms of the disparate molecular and apparatus length scales implicit in the respective equations governing their behavior, coupled with the fact that the limiting behavior of the pertinent fields is singular in the ‘‘continuum limit,’’ where the ratio of these two length scales goes to zero. Despite our criticism, it would be erroneous to conclude that we believe molecular dynamical simulations to be devoid of utility in continuum-mechanical contexts. Rather, molecular dynamics has a clearly defined complementary role to play in terms of those aspects of continuum-level modeling that aim to go beyond purely phenomenological approaches to transport phenomena. Such modeling can be effected through hybrid computations, viz., those that jointly employ both molecular dynamic simulations and continuum descriptions of the same physical phenomena, each, however, in different spatial domains relative to their respective distances from the wall.

Computations of this nature closely reflect the spirit of the singular perturbation scheme outlined in Sec. II. Explicitly, in hybrid computations, molecular-level simulations are employed near the wall, wherein the effect of the molecular forces is explicitly simulated by using a Langevin equation (or some alternative variation thereof), incorporating the wall forces directly into the simulations. Such computations are then matched (at an average level) onto the continuum-scale fields in an overlap region. The latter domain is situated at a sufficient distance from the wall such that the wall interaction forces with the fluid effectively vanish, thereby allowing for a smooth matching with the outer-scale continuum fields. Temporal and spatial evolution of these continuum-scale fields can then be simulated by dealing directly with the conventional phenomenological transport equations, presumed to be applicable in the absence of wall effects. In this manner one computationally simulates the formal matching procedure required in the singular perturbation analysis. Such simulations would, in principle, obviate the need for continuum-scale boundary conditions, auxiliary continuum-scale surface-excess fields and fluxes, and the like. The resulting continuum scale distributions thereby obtained would then display complete consistency with the molecular-level l-scale phenomena occurring near the wall, as well as with the L-scale phenomena occurring far from the wall compared with molecular dimensions. We are aware of only a very few such studies that explicitly embody these hybrid procedures [29,30].

V. SUMMARY

This contribution has reexamined the classical continuum-mechanical concepts of ‘‘boundary conditions,’’ as well as the closely related issue of ‘‘surface fields,’’ in the context of a simple model of molecular-scale phenomena. This model dealt with the purely diffusive transport of spherical Brownian solute particles (colloidal ‘‘molecules’’) dispersed in a viscous solvent bounded laterally by solid plane walls. Potential-energy wall-interaction forces were explicitly accounted for in the transport equations, as too were purely steric hydrodynamic wall effects inhibiting the mobility of the Brownian particles near the wall. While the validity of such an elementary model for describing true molecular-scale phenomena might be questioned, simulations demonstrating the validity of Stokes law at the molecular scale [63] (wherein similar questions might be raised) lend credibility to our model, as well as to the accompanying physical reasoning.

Using this elementary transport model we clarified the fundamental distinction existing between continuum-mechanical boundary conditions and the literal molecular-scale statistical-mechanical conditions prevailing at a solid wall. We showed unequivocally that these two types of ‘‘conditions’’ are, in general, completely different, possessing very different physical interpretations. Explicitly, we used singular perturbation analysis to argue formally that continuum-scale boundary conditions represent the asymptotic, outer limit of the more exact physical description of the transport processes, whereas the molecular-scale conditions prevailing at the wall embody the inner limit of the exact physics. In order to emphasize our fundamental contention that *conditions at a boundary are not boundary conditions* we coined the phrase ‘‘molecular wall effects.’’ This phraseology was meant to direct attention to the existence of a molecular analog of hydrodynamic wall effects. At the same time, just as the diminished mobility of those non-Brownian spheres in a neutrally buoyant suspension that are either in direct contact with, or closely proximate to, its bounding surfaces is irrelevant to the gross rheological properties of the flowing suspension, so too is the comparable immobility of molecules proximate to solid boundaries irrelevant to the gross rheological properties of homogeneous fluids composed of these molecules. As such, we are of the opinion that the molecular dynamic simulation [2] claiming to demonstrate the validity of the classical no-slip *convective* boundary condition for homogeneous viscous fluids is spurious, amounting instead to a demonstration of the existence of molecular wall effects, rather than constituting a valid computational ‘‘proof’’ of the macroscale adherence condition.

Our analysis also clarified the basic physical principles underlying adsorption concepts, such as surface concentration and surface diffusion, as being dependent upon the scale of observation of the phenomena in relation to the effective length scale of the molecular forces. It was argued that these surface fields do not, in a literal physical sense, represent either the true areal surface density or the surface velocity, respectively, of an adsorbed species at the wall. Rather, they arise from the need to rectify the disparity existing between the spatial domains of validity of the macroscale continuum phenomena (which do not quantify the correct physics near the wall owing to their failure to embody *s-f* forces) and the wall-scale physics.

ACKNOWLEDGMENTS

This work was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy, as well as by the Mathematical, Information and Computational Sciences Division within the Office of Computational and Technology Research of the Office of Energy Research of the D.O.E. We are grateful to Professor R. Jackson and Professor R. F. Sekerka for valuable discussions and encouragement.

---

[1] J. Koplik and J. R. Banavar, Annu. Rev. Fluid Mech. **27**, 257 (1995).

[2] J. Koplik, J. R. Banavar, and J. F. Willemsen, Phys. Fluids A **1**, 781 (1989).

[3] J. Koplik and J. R. Banavar, Phys. Rev. Lett. **80**, 5125 (1998).

[4] P. A. Thompson and S. M. Troian, Nature (London) **389**, 360 (1997).

[5] G. K. Batchelor, *An Introduction to Fluid Dynamics* (Cambridge University Press, Cambridge, England 1970).

[6] V. Ganesan and H. Brenner, Phys. Rev. Lett. **82**, 1333 (1999).

[7] J. Koplik and J. R. Banavar, Phys. Rev. Lett. **82**, 1334 (1999).

[8] D. A. Noever, Phys. Fluids A **2**, 858 (1990).

[9] R. Jackson, *Transport in Porous Catalysts* (Elsevier, New York, 1977).

[10] T. Graham, Philos. Mag. **2**, 175 (1833); **2**, 269 (1833); **2**, 351 (1833).

[11] H. R. Kramers and J. Kistemaker, Physica (Amsterdam) **10**, 699 (1943).

[12] J. Camacho and H. Brenner, Ind. Eng. Chem. Res. **34**, 3326 (1995).

[13] R. S. Perera and R. F. Sekerka, Phys. Fluids **9**, 376 (1997).

[14] T. Y. Liao and D. D. Joseph, J. Fluid Mech. **342**, 37 (1997).

[15] G. Mo and F. Rosenberger, Phys. Rev. A **44**, 4978 (1991).

[16] J. C. Maxwell, *Scientific Papers* (Dover, New York, 1962), Vol II, p. 681; Philos. Trans. R. Soc. London **170**, 231 (1879).

[17] Mo and Rosenberger [15] do, however, use molecular dynamic simulations to study a length-scale issue different from that addressed in the present paper, namely, one involving the ratio of the mean free path between successive intermolecular collisions in gases to the length scale characterizing the amplitude of their atomically ‘‘rough’’ walls. Their length-scale topic is, however, not directly pertinent to our analysis, although we do later briefly consider ‘‘macroscopic’’ surface roughness effects in relation to continuum boundary conditions. As an aside, while these authors’ simulations are concerned with gases of different molecular masses, one isolated—but relevant—case studied by them did involve equal molecular weight gases. Interestingly, they conclude in that case that the individual species do ‘‘slip’’ at the wall (as was equally true of all of their more extensive calculations involving components of differing molecular weights). It is not clear, however, that their finding of component slip in this case can be construed as lending support to our general conclusions regarding such slip, since in our terminology their ‘‘slip’’ would be classified as a ‘‘molecular wall effect,’’ rather than constituting a true continuum-level slip.

[18] The term ‘‘fluid’’ here includes both the interstitial solvent and the Brownian solute particles. Together, they constitute the binary fluid system that we analyze.

[19] In principle, one may also need to include in the simulation the solid-solid intermolecular force length scale l_{ss} too, the latter representing the range of the intermolecular forces acting between the molecules of which the wall is composed. If so, we implicitly assume in what follows that this additional length scale is of the same order as l_{ff} and l_{sf}.

[20] In continuum mechanics, constitutive equations represent the *intrinsic* response of an effectively unbounded system to a ‘‘stress.’’ This response is quantified by both the form of the constitutive relation and the material phenomenological coefficients appearing therein, the latter material parameters depending only upon the intrinsic *f-f* molecular physicochemical nature of the fluid. In particular, such parameters are independent of the boundary conditions, and hence also of the nature of the *s-f* forces.

[21] Indeed, refined microscale continuum-mechanical equations do not generally require the specification of boundary conditions at solid walls, since satisfaction of such conditions is automatically assured by virtue of the ‘‘exactness’’ of these modified $(l \oplus L)$-scale equations in quantifying the detailed microphysics in proximity to the walls (as well, of course, as everywhere else in the fluid continuum).

[22] In this specific context, however, we need to indicate the possibility of obtaining more accurate continuum-mechanical representations of the physics existing in those regions near to the walls by direct incorporation of these wall effects into the derivation of the continuum equations themselves. The studies by Ronis and co-workers [Physica A **88**, 215 (1977); **121**, 1 (1983)] represent attempts in this direction.

[23] W. Eckhaus, Matched Asymptotic Expansions and Singular Perturbations, (North-Holland, Amsterdam, 1973).

[24] M. Van Dyke, Perturbation Methods in Fluid Mechanics (Parabolic, Stanford, 1975).

[25] C. M. Bender and S. A. Orszag, Advanced Mathematical Methods for Scientists and Engineers (McGraw-Hill, New York, 1979).

[26] W. Eckhaus, Asymptotic Analysis of Singular Perturbations (North-Holland, Amsterdam, 1979).

[27] J. Kerkovian and J. D. Cole, Perturbation Methods in Applied Mathematics (Springer-Verlag, New York, 1981).

[28] D. R. Smith, Singular-Perturbation Theory (Cambridge University Press, Cambridge, 1985).

[29] S. T. O'Connell and P. A. Thompson, Phys. Rev. E **52**, R5792 (1995).

[30] N. G. Hadjiconstantinou and A. T. Patera, Int. J. Mod. Phys. C **8**, 967 (1997).

[31] S. Richardson, J. Fluid Mech. **59**, 707 (1973).

[32] S. Richardson, J. Fluid Mech. **49**, 327 (1971).

[33] P. G. Saffman, Stud. Appl. Math. **50**, 93 (1971).

[34] J. G. Kirkwood, Selected Topics in Statistical Mechanics (Gordon & Breach, New York, 1967).

[35] J. Happel and H. Brenner, Low Reynolds Number Hydrodynamics (Kluwer, Dordrecht, 1983).

[36] S. Chandrasekhar, Rev. Mod. Phys. **15**, 58 (1943).

[37] S. Kim and S. Karrila, Microhydrodynamics (Butterworth-Heinemann, Newton, MA, 1991).

[38] This functional dependence, as well as that of the potential energy field E, neglects effects arising from the presence of the second wall at $y^*=2L_y$. By virtue of the geometric symmetry of the system, such effects could easily have been incorporated into the present analysis, modulo a heightened degree of notational complexity.

[39] A. Einstein, Theory of Brownian Motion (Dover, New York, 1956).

[40] H. Brenner, J. Colloid Interface Sci. **23**, 407 (1967).

[41] More explicitly, using the known creeping flow mobilities of a torque-free, freely rotating sphere almost in contact with a plane wall, we have for the usual no-slip case that $D_\parallel/D_\infty = 2\{\ln[a/(y^*-a)]\}^{-1}$ [A. J. Goldman, R. G. Cox, and H. Brenner, Chem. Eng. Sci. **22**, 637 (1967)] and $D_\perp/D_\infty = 2(y^*-a)/a$ [R. G. Cox and H. Brenner, *ibid.* **22**, 1753 (1967). For the comparable slip case, where slip occurs on the plane and/or the sphere, see A. M. J. Davis, M. T. Kezirian, and H. Brenner, J. Colloid Interface Sci. **165**, 129 (1994) for the corresponding wall-corrected Stokes-Einstein diffusivities.

[42] R. B. Bird, W. E. Stewart, and E. N. Lightfoot, Transport Phenomena (Wiley, New York, 1960).

[43] Since the mass-average velocity of the fluid is zero in the present problem, and since the solute and solvent have been assumed to possess the same mass densities (owing to their neutral buoyancy), it follows from Eq. (10) that the microscale *solvent* velocity also vanishes at the wall.

[44] Our refinement of the continuum-mechanical equation, and its appellation as ''exact,'' should not necessarily be strictly construed as suggesting an exact one-to-one correspondence with the corresponding statistical-mechanical molecular description of the diffusional processes in the presence of wall-interaction forces. For we have *assumed* the applicability of a Fickian-type constitutive law, embodying a position-dependent anisotropic diffusivity (as well as a physicochemically induced potential-energy wall-fluid force) to describe the diffusional process. However, the presence of steep gradients in density might invalidate the linear response approach of Fick's law, thereby necessitating higher-order (or, possibly, density-functional) constitutive equations. Nevertheless, our goal in this article is not to derive accurate boundary conditions for the wall, but rather to clarify the concept of continuum-mechanical boundary conditions via a simple illustrative example. If an alternative constitutive formulation (accounting for the steep density gradients) can be found, then the procedure to be outlined subsequently still prescribes a rational scheme enabling continuum-mechanical boundary conditions to be systematically derived.

[45] For instance, the first case would require us to deal first with the regime $\{y/\delta\sim O(1),\ y/\epsilon\ll 1\}$, followed by the regime $\{y/\delta\gg 1,\ y/\epsilon\sim O(1)\}$.

[46] H. Brenner and L. G. Leal, J. Colloid Interface Sci. **88**, 136 (1982).

[47] The scope of the present paper is concerned only with the leading-order fields, inasmuch as this degree of accuracy proves sufficient to support our claims regarding the relationship between the literal, microscale conditions prevailing at a boundary and the conventional macroscale boundary conditions. As such, it is unnecessary to formally calculate higher-order terms in either the outer perturbation expansion (31) or its inner counterpart (38), although this could readily be done via the apparatus of singular perturbation theory, modulo the expenditure of the requisite algebraic effort.

[48] In a similar vein, comparable matching of the inner and outer tangential flux components based upon Eqs. (53), (54), and (59) yields the following zero-order outer tangential flux ''condition at the boundary:'' $J_x^0(x,y=0)=D_\infty(P_1-P_2)$. This result accords with the first of the intuitively derived equations (27), which applies for all y. It demonstrates, of course, the scale dependence of such a ''condition,'' our main contention.

[49] It is also interesting to note from Eq. (53) that $\tilde{J}_x^0(x,\tilde{y}) = D_\parallel(\tilde{y})(P_1-P_2)\exp[E_\infty-E(\tilde{y})]$. However, at large distances from the wall, we expect the parallel component $D_\parallel$ of the diffusivity and the potential E to adopt constant (y-independent) values, $D_\parallel(\tilde{y}\to\infty)\to D_\infty=1=\text{const}$; $E(\tilde{y}\to\infty)\to E_\infty=\text{const}$. Consequently, we find that, asymptotically, $\tilde{J}_x^0(x,\tilde{y})\cong D_\infty(P_1-P_2)=\text{const}$ for $\tilde{y}\ll\delta$, i.e., in the outer region. The latter equation should be compared with the outer equation (27).

[50] K. A. Jansons, Phys. Fluids **31**, 15 (1988).

[51] That paper, begun with the continuum-scale Navier-Stokes equations and with a prescribed boundary condition at the rough wall, does not explicitly include wall-interaction forces.

[52] H. Brenner and L. G. Leal, J. Colloid Interface Sci. **62**, 238 (1977).

[53] We focus our discussion exclusively on continuum-mechanical surface transport phenomena, thereby eschewing the theoretical possibility of molecular-level adsorption onto, and diffusion along, the wall.

[54] H. Brenner, J. Colloid Interface Sci. **68**, 422 (1979).

[55] G. M. Mavrovouniotis and H. Brenner, Philos. Trans. R. Soc. London, Ser. A **345**, 165 (1993).

[56] V. Ganesan and H. Brenner, Proc. R. Soc. London, Ser. A **456**, 731 (2000).

[57] D. A. Edwards and H. Brenner, Interfacial Transport Processes and Rheology (Butterworth-Heinemann, Newton, MA, 1991).

[58] M. Shapiro, H. Brenner and D. C. Guell, J. Colloid Interface Sci. **136**, 552 (1990).

[59] ''Adsorption'' as an *intrinsic* objective physicochemical property of the dual molecular natures of the solid wall and fluid

alone, independently of the dimensions of the apparatus in which the adsorption occurs, is a strictly asymptotic concept. Erroneous opinions to the contrary can be traced to a failure to distinguish clearly between ‘‘surface’’ and ‘‘surface-excess’’ areal densities. Only the latter represents a correct physical concept. Thus, for example, describing some species as being ‘‘weakly adsorbed’’ in an attempt to quantify some objective intrinsic physicochemical property of the binary fluid/solid-wall system, independently of the dimensions of the container in which the adsorption experiment is conducted, is a meaningless, and indeed misleading concept—an oxymoron. Adsorption, at least *linear* adsorption, is quantified by an intrinsic molecular length scale l_m, implicitly embodied in the magnitude of the Henry’s law constant. The latter length scale, intermediate in magnitude between the molecular scale l_{ff} and the macroscopic apparatus scale L, appears naturally as a consequence of the proportionality between an areal or surface density (mass or molecules per unit *area*) and a volumetric or bulk density (mass or molecules per unit *volume*). Surface(-excess) adsorption is thus necessarily quantified by the nondimensional ratio l_m/L—which, being dependent upon the linear dimension L of the apparatus normal to the wall on which the adsorption measurement is being performed, is clearly not an intrinsic material physicochemical property of the system, independently of the magnitude of L, except in the singular asymptotic limit $l_m/L \to 0$. This point of view points up the impossibility of molecular dynamic simulations being able to provide values of the Henry’s law adsorption coefficient without the computational ability to probe the ‘‘outer’’ continuum-mechanical region.

[60] In circumstances where the potential-energy well in Fig. 2 is very deep, only the region in the immediate vicinity of $y^* = l_m$ contributes to Eq. (78), whence the (dimensional) surface diffusivity is given by $D_s^* = D_\parallel^*(y^* = l_m)$. For a specified value of l_m the latter dimensional volumetric diffusivity component can thus be estimated from the requisite expression cited in Ref. [41].

[61] L. H. Dill and H. Brenner, J. Colloid Interface Sci. **85**, 101 (1982).

[62] H. Brenner and D. A. Edwards, Macrotransport Processes (Butterworth-Heinemann, Newton, MA, 1993).

[63] J. Koplik and J. R. Banavar, Phys. Rev. Lett. **75**, 232 (1995).